Characteristics of Multi-Solute Adsorption in Dilute Aqueous Solution(Dissertation_全文)

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CHARACTERISTICS OF MULTI-SOLUTE ADSORPTION IN DILUTE AQUEOUS SOLUTION

HIROYUKI KAGE

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CHAPTER 1

INTRODUCTION

1-1 Historical Review and Abstract of This Thesis

Current interests in removing pollutants from industrial and municipal wastewaters have stimulated investigations of adsorption process for water purification. In the design of such purification facilities, the information of multi-solute adsorption equilibrium is essential, and it is desirable to predict the adsorption behaviors of mixed solutes in dilute aqueous solution employing only experimental data of each single-solute adsorption, and further only experimental data which are described in terms of the total concentration of the solution when it contains many unknown solutes. In spite of this industrial importance, little attention has been paid.

The first attempt for prediction of multi-solute adsorption equilibrium was performed by Ockrent[11)]

and Weber[17]. They extended the Langmuir equation for single-solute to multi-solute system. Radke and Prausnitz[12] have proposed a prediction method which was based on a formulation of thermodynamics of adsorption, and obtained good results for the adsorption equilibria of acetone - propionitrile and p-cresol - p-chlorophenol aqueous solutions by activated carbon. Further recently Jossens et al.[7] improved the method proposed by Radke and Prausnitz[12]. On the other hand, Rosene et al.[13,14] have applied the Polanyi potential theory to many single-solute systems, and recently extended it to two or three-solute competitive adsorption systems. Some methods for the prediction of multi-solute adsorption equilibrium were introduced above, but they respectively have disadvantages. The further development for this purpose should be needed.

On the other hand, adsorption rate as well as equilibrium is one of the most important factor for adsorption operation. The design of purification facilities is performed by the combination of the two factors, that is, adsorption equilibrium and rate. Some principal papers published till now, which referred to adsorption rate or multi-component fixed-bed

adsorption, are as follows.

Hashimoto et al.[6] and Suzuki et al.[15] calculated numerically the adsorption rate for batch operation in the case of pore or surface diffusion kinetics. Brecher et al.[1,2] and Neretnieks[10] also calculated the rate curves of the concentration change for the system, in which both pore and surface diffusion effects could not be neglected.

Cooney et al.[4] calculated approximately the breakthrough curve of multi-solute fixed bed adsorption under the Langmuir type adsorption equilibrium and constant pattern approximation. Further Carter et al.[3] and Gariepy et al.[5] carried out the breakthrough analysis of the binary adsorption using gas mixtures.

Kawazoe[8], Takeuchi et al.[16] and Miura et al.[9] experimentally obtained the breakthrough curves for two or three-solute aqueous solutions, and Takeuchi et al.[16] presented a simplified method for calculating the breakthrough time and the length of adsorption zone. Miura et al.[9] also proposed a simplified method for calculating the breakthrough curve of two-solute system under the constant pattern and linear driving force approximations.

However, all papers mentioned above, deal with

the adsorption systems which involve two or three known solutes, so that it is necessary to study the adsorption equilibrium and adsorption rate of wastewater which contains many unknown solutes.

The purposes of this thesis are to predict simply the adsorption equilibrium of mixed solutes in relatively dilute aqueous solution, to analyze the characteristics of adsorption equilibrium of wastewater which involves many unknown solutes and further to describe the characteristics of adsorption rate of such a wastewater in terms of the same concept.

In Chapter 2, a new method which employs a modified Langmuir kinematic adsorption model is proposed, assuming that the adsorptive surface is heterogeneous in adsorption energy. Multi-solute adsorption equilibrium can be predicted by the model from respective single-solute adsorption isotherms. The predictions of adsorption equilibria on activated carbon for ten kinds of aqueous solutions which involved two solutes, were performed. The prediction accuracy of the present method was the same or a little better and also the calculation procedure was much simpler than the two modified Radke's method,

which were proposed by Jossens et al. recently.

In Chapter 3, a new approximate description of adsorption equilibrium of wastewater containing a number of unknown pollutants was developed. In this description, the term of such a comprehensive index of concentration as TOC, BOD or COD can be used instead of the concentrations of each components. The description is constructed on the basis of a new concept, "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration", which is to be identified by the observed equilibrium data of the wastewater. The adsorption equilibria, which are predicted by the proposed description using the identified characteristic distribution of Langmuir coefficient, are agreed well with the experimental results.

In Chapter 4, the similar concept to "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration", proposed for adsorption equilibrium of wastewater in Chapter 3, is applied to analyze the adsorption rate of wastewater, and a new approximate description of adsorption rate is developed. By this description, the rate curves of concentration change of batch adsorption process are predicted exactly,

and the obtained volumetric coefficients of intra-particle mass transfer are consistent with the experimental data proposed in the past.

Chapter 5 presents conclusive remarks throughout this thesis and the problems to be solved in future.

1-2 Publications on This Thesis

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CHAPTER 3 : Journal of Chemical Engineering of Japan, 14, 26 (1981)

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CHAPTER 2

PREDICTION OF LIQUID PHASE ADSORPTION EQUILIBRIA OF MULTI-SOLUTES IN WATER

2-1 Introduction

Use of purification process by adsorption for industrial and municipal wastewater treatment has been more prevalent in recent years. Adsorption equilibria for mixtures of organic pollutants are required for design of these processes. To reduce experimental work, it is desirable to be possible to predict the adsorption equilibrium of mixed organic solutes in dilute aqueous solution employing only experimental data from the single-solute adsorption isotherms.

In spite of its industrial importance, there are few studies on the method of prediction or correlation of multi-solute adsorption equilibrium. Ockrent[3] and Weber[8] employed the Langmuir model

extended to multi-solute system to predict two-solute adsorption. But their extended Langmuir model has a strong limitation on its application, because only few organic aqueous solutions follow the Langmuir isotherm. Radke and Prausnitz[4] extended the method of Myers and Prausnitz[2], which was proposed for mixed-gas adsorption, to multi-solute adsorption from dilute liquid solution. Their method is based on a formulation of the thermodynamics of adsorption, and it seems to be the most reliable one at present. Although, recently, Jossens et al.[1] further improved its accuracy of prediction by applying their own correlation formula to single-solute adsorption isotherm, the model still has some ambiguity in the accuracy. On the other hand, Rosene et al.[5] developed a calculation method of the physical adsorption of solids on activated carbon from multi-component solutions using the adsorption isotherms of the individual components on the basis of the Polanyi adsorption potential theory. Although their method is well adapted for estimating the adsorption of traces of one component from high concentrations (up to near-saturation) of another, it requires further investigations for extension to the competi-

tive adsorption among the components having concentrations in the same order.

In this chapter, a new method which employs a modified Langmuir kinematic adsorption model is proposed, assuming that the adsorptive surface of adsorbent is heterogeneous in energy of adsorption.

2-2 Correlation of Single-Solute Adsorption Isotherm

We recognize a heterogeneous surface of adsorbent to be described by a distribution of adsorption energy. Each "patch" of surface characterized by a given potential becomes the seat of an adsorbed phase, so that the surface is composed of infinitesimal patches of different energy. Now the Langmuir model (monolayer adsorption) is adopted on these individual patches, and further the following assumptions are made.

Assumptions:

1. These patches adsorb independently of one another.
2. The Langmuir equation holds for each of these patches.

$$\theta = Q_k/Q_{sk} = kC/(1+kC) \qquad (2\text{-}1)$$

3. The ultimate uptake capacity Q_s is characterized by the combination of adsorbent and adsorbate. Then it is assumed that the configuration of adsorbed molecules is much the same as that of the molecules in liquid state, and that it does not take any orientation. As the result, the surface area occupied by an adsorbed molecules can be approximated by the base area of a cube whose volume is as same as one occupied by a adsorbate molecule in liquid state. Therefore, Q_s is

$$Q_s = S/q_m N_v = S/N_v(M/\rho N_v)^{2/3} \qquad (2\text{-}2)$$

2-2-1 Definition of the energy distribution function on adsorption surface

The Langmuir coefficient "k" in Equation (2-1) can be regarded as a function of adsorption energy. It becomes large, as energy becomes large. Therefore let the value of k designate the adsorption energy level. Introducing the distribution function of the patches against k, f(k), the number of adsorption sites, which have energy level between k and

k+dk, per unit weight of adsorbent, can be described by f(k)dk. The total number of adsorption sites is given by Equation(2-3).

$$Q_s = \int_{k_{min}}^{k_{max}} f(k)dk \qquad (2-3)$$

The amount of adsorption on the patches which has adsorption energy level k, q(k,C) is given by

$$q(k,C) = f(k)kC/(1+kC) \qquad (2-4)$$

or integration of Equation(2-4) with respect to k, gives

$$Q(C) = \int_{k_{min}}^{k_{max}} q(k,C)dk = \int_{k_{min}}^{k_{max}} f(k)kC/(1+kC)dk \qquad (2-5)$$

Finally, adsorption isotherm for single-solute system is represented by Equation(2-5).

The next problem is how to identify the energy distribution function f(k) from the adsorption isotherm measured experimentally for single-solute system.

2-2-2 Identification of energy distribution function, f(k)

To determine f(k), so as to fit the experimental data of single-solute adsorption equilibrium, Q(C) in Equation(2-5), is essentially the same as "to solve an integral equation". There are various methods to solve integral equations, but for simplicity of the following calculations, in the present study, an analytical simulating formula which involves some unknown adjusting parameters was assumed as f(k), and the parameters which satisfied Equation(2-5) were numerically searched. (When the density of adsorbate, ρ, is unknown, Q_s becomes an unknown parameter, too. In this case, there are three unknown parameters to be identified as mentioned later.)

The next problem is how to choose an approximate formula for f(k). We can roughly consider about this problem as the following. If the adsorption sites which have very low adsorption energy are taken into account, the number of sites draw toward infinity in general. And the intrinsic distribution curve of sites is thought to start from a certain maximum value of k and to increase gradually as k decreases, as the curve A in Figure 2-1. Further the curve goes to infinity as k approaches 0, because there are sites, which have zero energy, everywhere on the

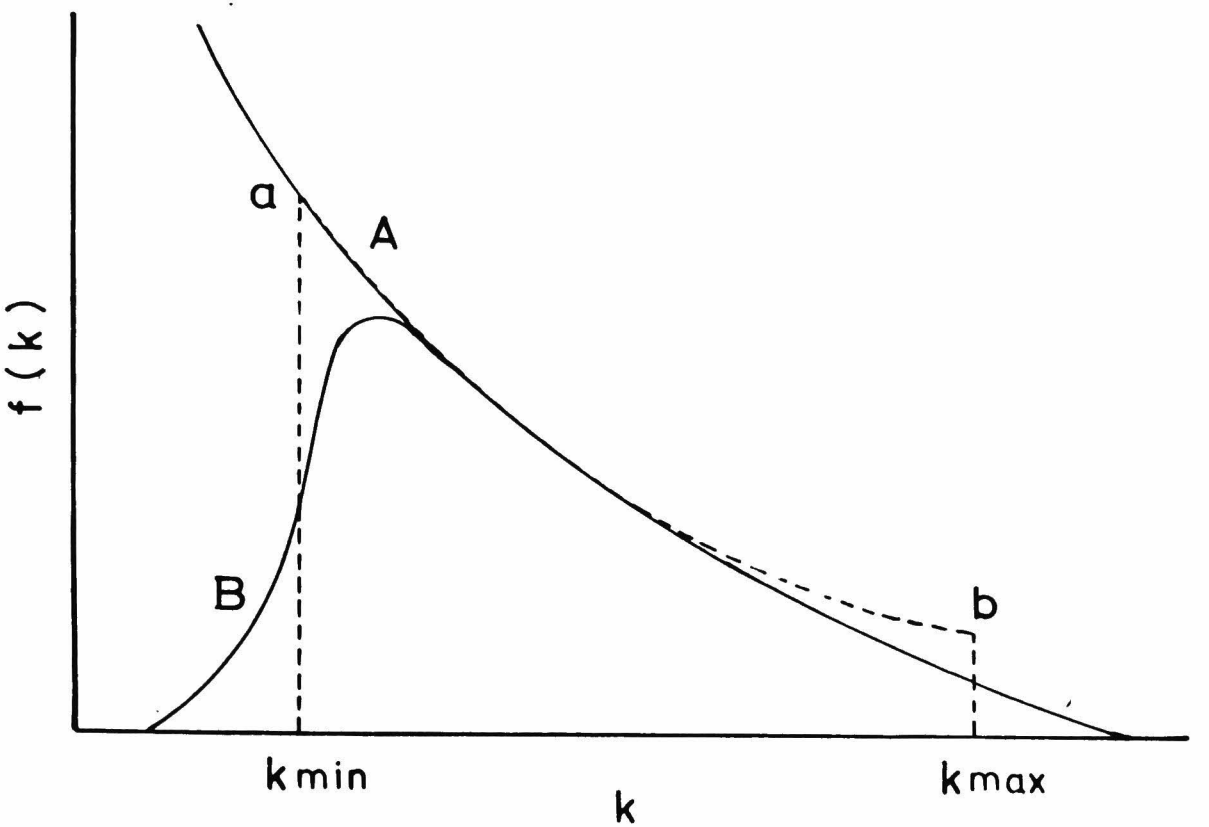


Fig.2-1 Distribution of energy of adsorption sites

adsorption surface. However, molecules adsorb on the sites from k_{max} to k_{min} in order of adsorption energy k, and a molecule occupies the finite area around the site. Therefore some sites which have lower value of k are covered with the adsorbed molecule which adsorbed on a higher k site and lose their adsorption capacity. According to the above consideration, the apparent distribution curve of patch for k increases gradually as k decreases from k_{max}, and has a maximum of f(k). Then it suddenly decreases as soon as it passes the maximum, and approaches f(k) = 0, as k decreases. The form of the curve is qualitatively illustrated by the curve B in Figure 2-1.

Although the various simulating formulas may be used for curve B in principle, Equation(2-6) which corresponds to the broken line a-b in Figure 2-1 is acceptable for the present problem from considerations of simplicity of analysis in spite of a little fault for accuracy of fitting.

$$f(k) = A/k \qquad k_{min} < k < k_{max} \tag{2-6}$$

There are three unknown adjusting parameters, A, k_{min} and k_{max} in Equation(2-6).

Substituting Equation(2-6) into Equation(2-3), we can get

$$Q_s = \int_{k_{min}}^{k_{max}} f(k)dk = A \ln(k_{max}/k_{min}) \qquad (2\text{-}7)$$

Equation(2-7) can be used to eliminate one parameter, A. Consequently the unknown parameters become k_{min} and k_{max}. Substitutions of Equations(2-6) and (2-7) into Equation(2-5) and the integration of Equation (2-5) with respect to k, give

$$Q(C) = \frac{Q_s}{\ln(k_{max}/k_{min})} \ln \frac{1+k_{max}C}{1+k_{min}C} \qquad (2\text{-}8)$$

The optimum values of k_{min} and k_{max} should be determined by fitting Equation(2-8) to the experimental equilibrium data for single-solute system. When ρ is unknown, the optimum values of Q_s, k_{min} and k_{max} must be determined.

On the other hand, when we notice the following explanation, it can be found that Equation(2-8), which has been obtained from the assumption of f(k), Equation(2-6), is closely related to the Frumkin-Temkin equation for heterogeneous surface of adsorbent. Equation(2-8) has been derived from Equation (2-5), and when the Langmuir equation is held for

each patches which have an arbitrary Langmuir energy coefficient "k", k in Equation(2-5) is represented by Equation(2-9).

$$k = a \cdot \exp(E/RT_a) \tag{2-9}$$

Then Equation(2-5) can be rewritten as Equation(2-10).

$$Q(C) = \int_{E_{min}}^{E_{max}} f'(E) \frac{a \cdot \exp(E/RT_a)C}{1+a \cdot \exp(E/RT_a)C} dE \tag{2-10}$$

where

$$f'(E) = f(k)\left(\frac{a}{RT_a}\right)\exp(E/RT_a) = f(k)\frac{dk}{dE} \tag{2-11}$$

The value of $a \cdot \exp(E/RT_a)C/\{1+a \cdot \exp(E/RT_a)C\}$ in Equation(2-10) is 0.5 when $a \cdot \exp(E'/RT_a)C = 1$ or $E' = -RT_a \ln(aC)$. Further it is very close to 0 when $E < E'$, and 1 when $E > E'$. So for Equation(2-10) we can perform the same approximation as Roginsky did[6], and obtain Equations(2-12) to (2-15).

$$Q(C) = \int_{E'}^{E_{max}} f'(E)dE \tag{2-12}$$

where

$$E' = -RT_a \ln(aC) \tag{2-13}$$

or

$$Q(C) = \int_{k'}^{k_{max}} f(k)dk \tag{2-14}$$

where

$$k' = 1/C \tag{2-15}$$

Further Equation(2-14) can be rewritten as Equation (2-16).

$$Q(C) = \int_{1/C}^{k_{max}} (A/k)dk = A \ln(k_{max}C)$$

$$= \frac{Q_s}{\ln(k_{max}/k_{min})} \ln(k_{max}C)$$

$$= \lambda \ln(\mu C) \tag{2-16}$$

Equation(2-16) is the same as the Frumkin-Temkin equation. Practically, when $k_{max} >> 1$ and $k_{min} << 1$, Equation(2-8) agrees with Equation(2-16), so it is found that Equation(2-8) is closely related to the Frumkin-Temkin equation. The relationship between Equations(2-12) or (2-14) and f(k) or f'(E) is considered more minutely in Appendix.

2-3 Extension to Multi-Solute System

Let us proceed to develop the prediction method of n-solute (multi-solute) adsorption equilibrium on the basis of single-solute equilibria. Now the following assumptions are made to simplify the

succeeding calculations.

Assumptions:

4. The interaction among adsorbed molecules can be ignored irrespectively of the species of the molecules. That is, adsorbed molecules can act in their occupied place independently of other molecules.
5. Although each patch has its peculiar values of k correspondingly to the species of adsorbate respectively, the rank in the order of k among the patches is independent of the species of adsorbate.

2-3-1 Relationship among the values of k for each adsorbate

The accumulated number of patches from k^* to k_{max}, is given by

$$U(k^*) = \int_{k^*}^{k_{max}} f(k)dk \qquad (2\text{-}17)$$

When an arbitrary patch has adsorption energy k_1^* for adsorbate 1, k_2^* for adsorbate 2, and k_i^* for adsorbate i, the relationship among k_1^*, k_2^*, $\cdots$ k_i^* is described by Equation(2-18) according to the

assumption(5).

$$U_1(k_1^*)/Q_{s1} = U_2(k_2^*)/Q_{s2} = \cdots = U_n(k_n^*)/Q_{sn} \qquad (2\text{-}18)$$

This relationship is schematically illustrated in Figure 2-2. Combining Equations(2-7), (2-17) and (2-18), we get

$$\frac{\ln(k_{1,max}/k_1^*)}{\ln(k_{1,max}/k_{1,min})} = \frac{\ln(k_{2,max}/k_2^*)}{\ln(k_{2,max}/k_{2,min})} = \cdots = \frac{\ln(k_{n,max}/k_n^*)}{\ln(k_{n,max}/k_{n,min})} \qquad (2\text{-}19)$$

2-3-2 Langmuir adsorption isotherm for multi-solute system

Surface coverage for component i for homogeneous surface, θ_i, is

$$\theta_i = k_i C_i (1 - \sum_{j=1}^{n} \theta_j), \quad i = 1, 2, \cdots n \qquad (2\text{-}20)$$

Equation(2-20) can be solved with respect to θ_i to give Equation(2-21).

$$\theta_i = \frac{k_i C_i}{1 + \sum_{j=1}^{n} k_j C_j}, \quad i = 1, 2, \cdots n \qquad (2\text{-}21)$$

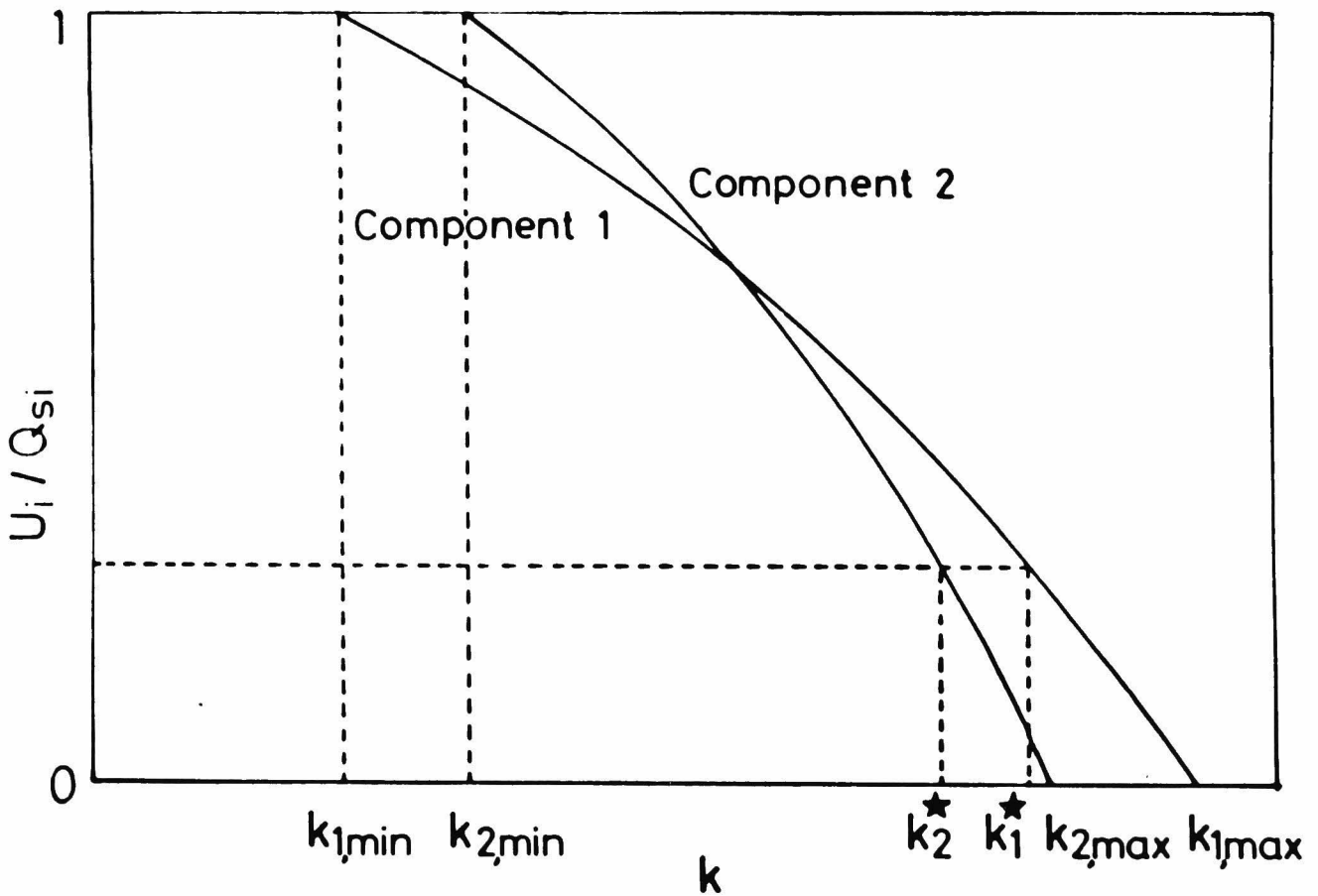


Fig.2-2 Relationship between k_1^* and k_2^*

On the other hand, the surface coverage for heterogeneous surface is

$$\theta_i(C_i,k_i^*) = \frac{k_i^* C_i}{1+\sum_{j=1}^{n} k_j^* C_j}, \quad i = 1, 2, \cdots n \qquad (2\text{-}22)$$

where k_i^* in Equation(2-22) should hold the relationship described by Equation(2-19). Finally the amount of adsorption for i, Q_i, can be expressed as follows.

$$Q_i(C_i) = \int_{k_{i,min}}^{k_{i,max}} f_i(k_i^*)\theta_i(C_i,k_i^*)dk_i^*$$

$$= \frac{Q_{si}C_i}{\ln(k_{i,max}/k_{i,min})} \int_{k_{i,min}}^{k_{i,max}} \frac{dk_i^*}{1+\sum_{j=1}^{n} k_j^* C_j},$$

$$i = 1, 2, \cdots n \qquad (2\text{-}23)$$

Further k_j^* in Equation(2-23) can be described as Equation(2-24) from Equation(2-19), by using k_i^*.

$$k_j^* = (k_i^*/k_{i,max})^{K_{ij}} k_{j,max} \qquad (2\text{-}24)$$

where

$$K_{ij} = \ln(k_{j,max}/k_{j,min})/\ln(k_{i,max}/k_{i,min}) \qquad (2\text{-}25)$$

Substituting Equation(2-24) into Equation(2-23), we get

$$Q_i(C_i) =$$

$$\frac{Q_{si}C_i}{\ln(k_{i,max}/k_{i,min})}\int_{k_{i,min}}^{k_{i,max}}\frac{dk_i^*}{1+\sum_{j=1}^{n}(k_i^*/k_{i,max})^{K_{ij}}k_{j,max}C_j} \qquad (2\text{-}26)$$

Since Q_{si}, $k_{i,min}$ and $k_{i,max}$, in Equation(2-26) can be obtained from experimental data for each solute, the amounts of adsorption for all solutes at arbitrary concentrations, C_i, can be calculated by using Equation(2-26).

2-4 Experiments

The experiments of adsorption equilibria on activated carbon (CAL, Calgon Corp.) for two-solute aqueous solution systems (phenol - p-nitrophenol, p-nitrophenol - p-cresol), were performed to verify the accuracy of the theoretical model. Before use, the carbon (14∿16 mesh) was crushed, and the powdered carbon under 200 mesh was adopted. The powdered carbon was further washed and dried at 110°C for a day. Finally it was kept in a desiccator containing silicagel. Adsorption equilibria were obtained by contacting known weights of carbon with a given

solution in flasks. The weight of carbon was 0.3g ∿ 1.0g and the volume of solution in flask was o.1ℓ ∿ 0.2ℓ. The carbon was degassed for 30 minutes by aspirator as soon as it contacted with the solution. The flasks were placed on a shaker and agitated for 1 ∿ 4 days at 35°C. After the equilibrium was attained, a sample was taken from each flask. Prior to analysis, it was filtered through a 0.5μ-glass filter to be free of any trace of suspended carbon. The concentration of each solute at equilibrium was measured by an ultraviolet spectrophotometry. The wave lengths of 269.5 and 317.0nm were used for phenol - p-nitrophenol system, and 276.5 and 317.0nm for p-cresol - p-nitrophenol system.

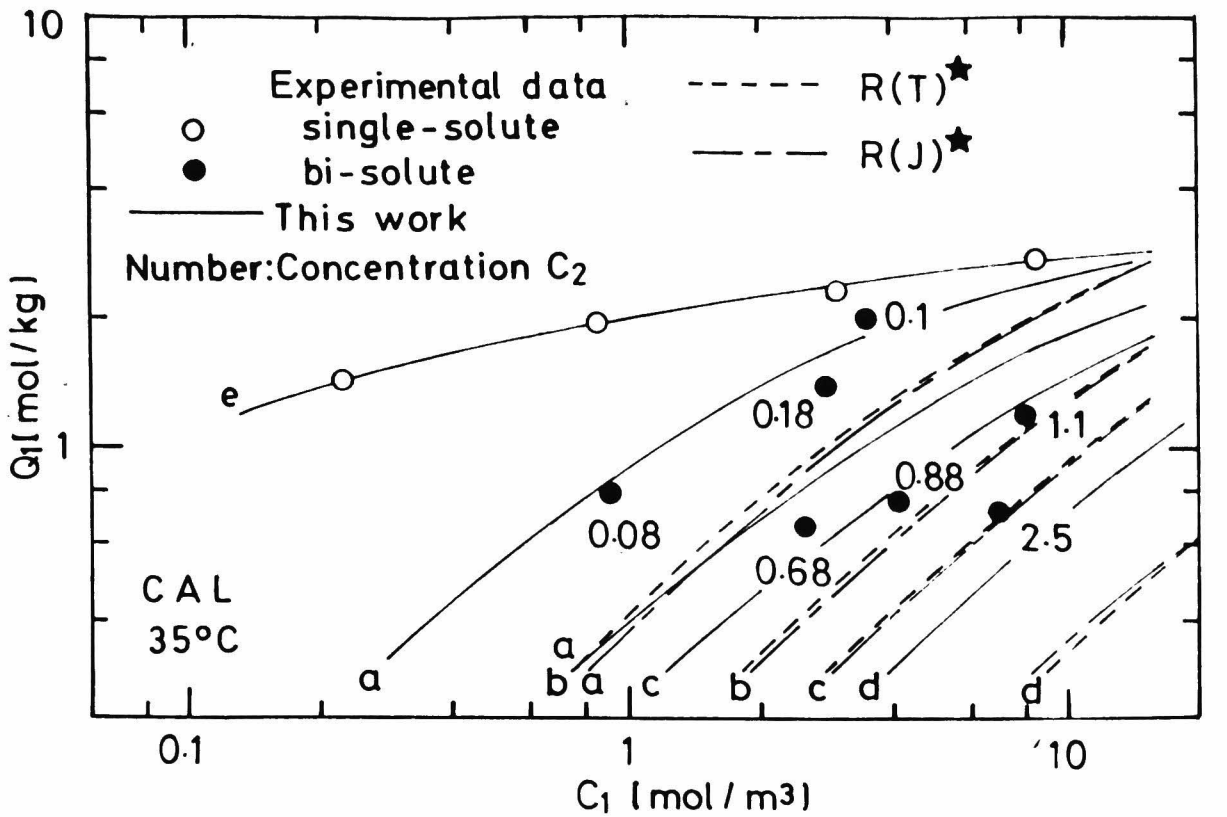
The equilibrium data for phenol - p-nitrophenol and p-cresol - p-nitrophenol system are shown in Figures 2-3 and 2-4, and Figures 2-5 and 2-6, respectively. Three kinds of curves in Figures 2-3 to 2-6 show the prediction results by the proposed method and two modified Radke's methods, and they will be explained in detail later.

2-5 Results of Prediction

In this section, the prediction of adsorption equilibria on activated carbon for ten kinds of adsorption system which involves two solutes, are performed by the three methods, namely two modified Radke's methods[1)], in which the Toth equation, and the Jossens equation are adopted respectively, and the present method. The adsorption systems used for the predictions are two bi-solute systems which were introduced in 2-4, six systems by Jossens et al., and two systems by Radke et al..

2-5-1 Determinations of parameters for single-solute systems

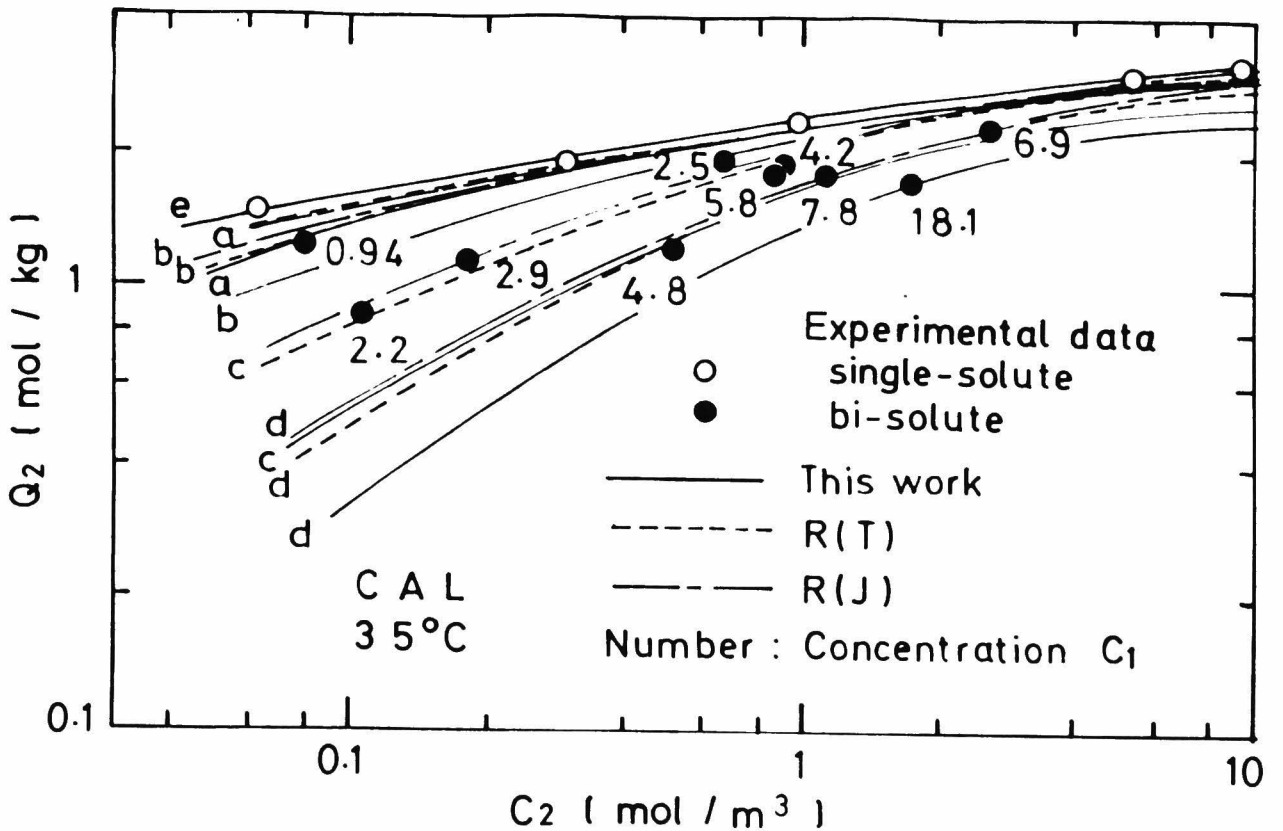
First let us determine the parameters by the method which was introduced in 2-2 using single-solute adsorption data. The ultimate uptake capacity, Q_s, can be obtained from Equation(2-2) using ρ, M and S (B.E.T. surface area), which were given in Table 2-1. And the calculated values of Q_s are also shown in Table 2-1. Q_s's for two systems, o-phenyl phenol and dodecyl benzol sulfonic acid could not be calcu-



(a)C_2=0.1, (b)C_2=0.5, (c)C_2=1.0, (d)C_2=5.0, (e)C_2=0.0[mol/m^3]

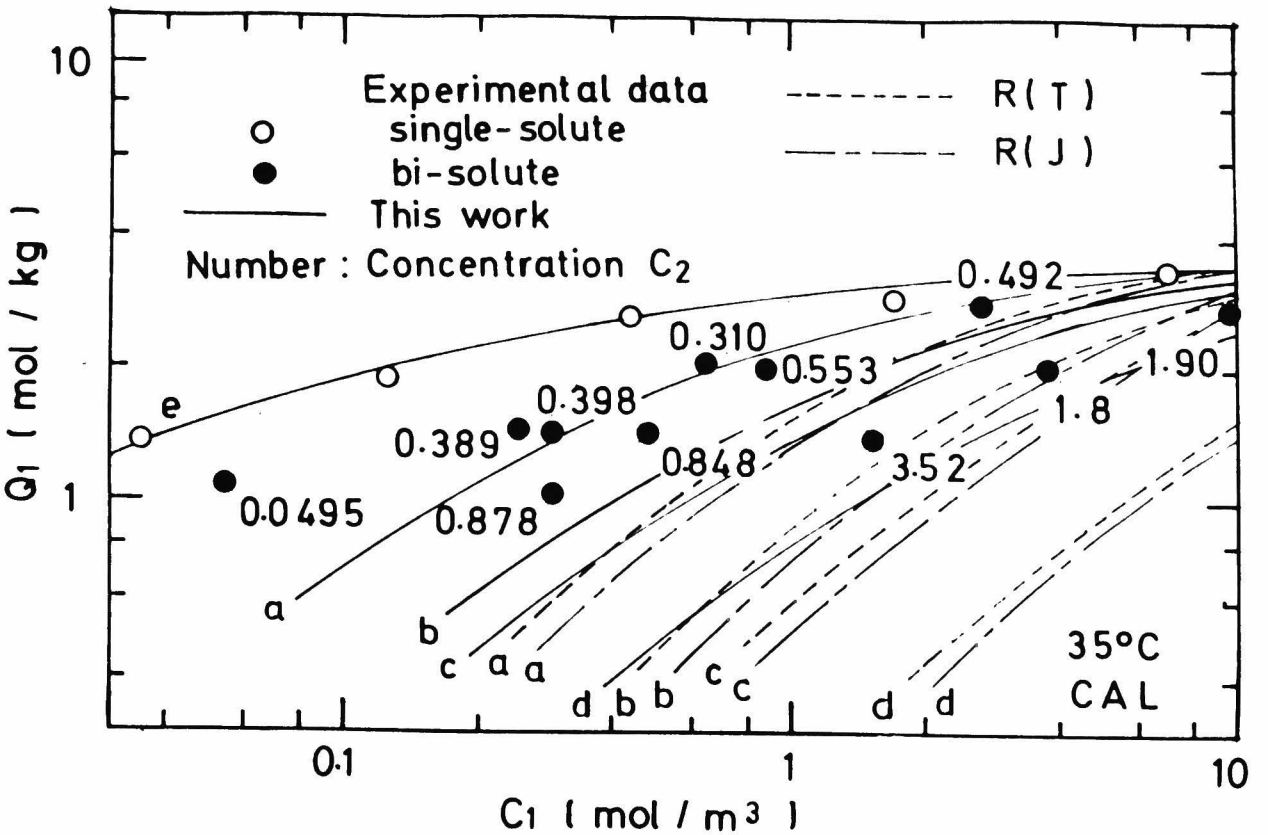
Fig.2-3 Adsorption isotherms of phenol(1) in the presence of p-nitrophenol(2)

* See d and e in Table 2-3.



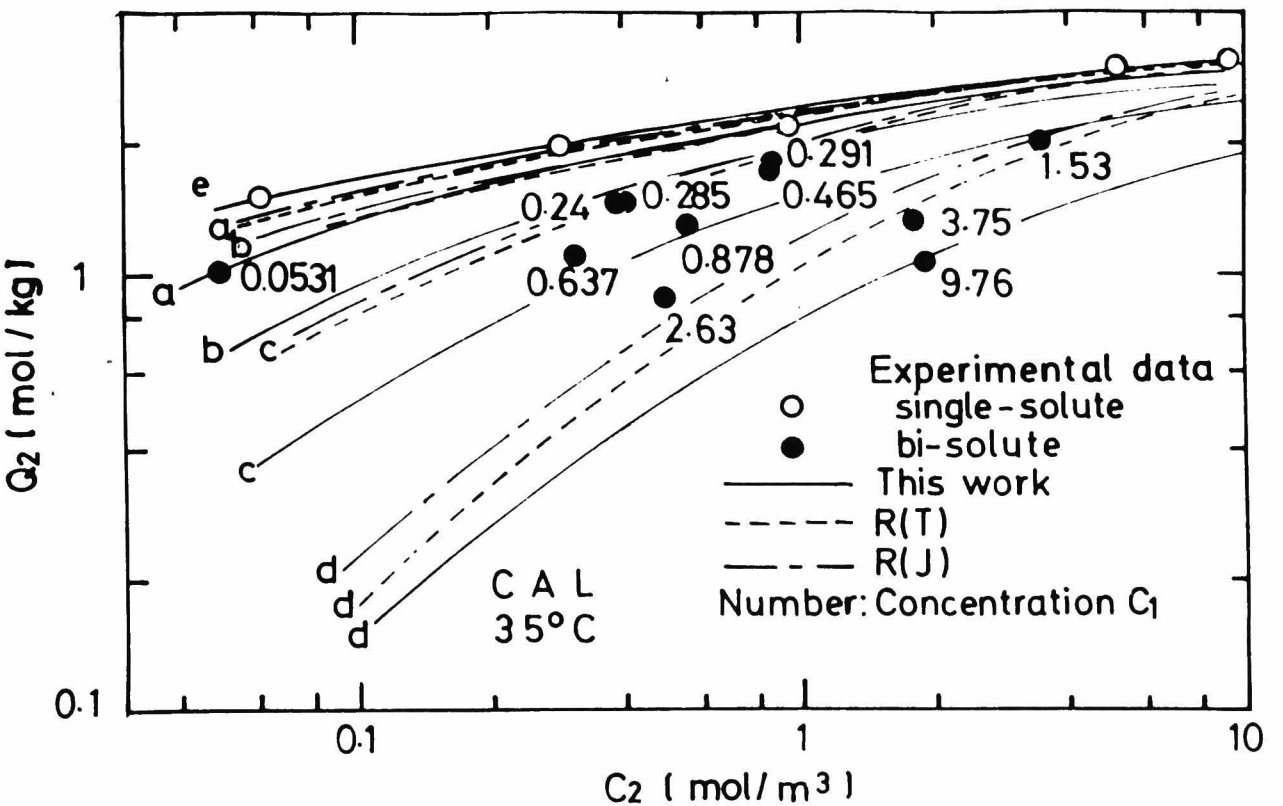
(a)C_1=0.5, (b)C_1=1.0, (c)C_1=5.0, (d)C_1=10.0, (e)C_1=0.0[mol/m^3]

Fig.2-4 Adsorption isotherms of p-nitrophenol(2) in the presence of phenol(1)



(a)C_2=0.1, (b)C_2=0.5, (c)C_2=1.0, (d)C_2=5.0, (e)C_2=0.0[mol/m^3]

Fig.2-5 Adsorption isotherms of p-cresol(1) in the presence of p-nitrophenol(2)



(a)C_1=0.1, (b)C_1=0.3, (c)C_1=1.0, (d)C_1=5.0, (e)C_1=0.0[mol/m^3]

Fig.2-6 Adsorption isotherms of p-nitrophenol(2) in the presence of p-cresol(1)

Table 2-1 Characteristic Properties of Adsorbent and Adsorbate, and Ultimate Uptake Capacity of Single-Solute System by Equation(2-2)

Solute	T	Activated carbon	$Mx10^{3}$	$Sx10^{-3}$	$\rho x10^{3}$*	Q_s	(***)
1**	35	CAL	94.11	920	1.06	5.48	b
2	35	CAL	139.11	920	1.48(20°C)	5.27	c
3	35	CAL	108.14	920	1.03(25°C)	4.89	d
1	20	B10-I	94.11	1500	1.07(25°C)	8.99	a
2	20	B10-I	139.11	1500	1.48	8.59	c
4	20	B10-I	128.56	1500	1.31	8.33	c
5	20	B10-I	122.12	1500	1.27(15°C)	8.45	a
6	20	B10-I	136.14	1500	1.09(77°C)	7.11	a
8	20	B10-II	163.01	1500	1.41(34°C)	7.50	b
3	25	Filtrasorb 300	108.14	1000	1.03	5.32	d
4	25	Filtrasorb 300	128.56	1000	1.27(28°C)	5.46	b
10	25	Filtrasorb 300	58.08	1000	0.785	6.72	d
11	25	Filtrasorb 300	55.08	1000	0.777	6.91	d

* When ρ of solute was not available at experimental temperature, available one at the nearest temperature were adopted. In such cases, the temperatures are put in parentheses.

Table 2-1 (continued)

** 1:phenol, 2:p-nitrophenol, 3:p-cresol, 4:p-chlorophenol, 5:benzoic acid, 6:phenyl acetic acid, 7:o-phenyl phenol, 8:2,4-dichlorophenol, 9:dodecyl benzol sulfonic acid, 10:acetone, 11:propionitrile

*** Literature cited

a) Kagaku Daijiten Hensyu Iinkai, "Kagaku Daijiten", Kyoritsu Shuppan, Tokyo, Japan (1961)

b) Kagaku Kogaku Kyokai, "Bussei Josu", vol.5, Maruzen, Tokyo, Japan (1967)

c) Lange, N. A., "Handbook of Chemistry", McGraw-Hill, New York, U.S.A. (1967)

d) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, New York, U.S.A. (1950)

lated, because their densities were not available. Next the values of parameters, k_{max} and k_{min}, were determined from the equilibrium data for single-solute systems, using the determined Q_s and Equation (2-8). For only two systems, o-phenyl phenol and dodecyl benzol sulfonic acid, whose Q_s could not be obtained, k_{max}, k_{min} and Q_s were searched as parameters. The parameters were searched by SIMPLEX method using Equation(2-27) as the performance index.

$$F = -\{(1/N) \sum_{i=1}^{N} (1-Q_{i,calc}/Q_{i,exp})^2\}^{1/2} \qquad (2\text{-}27)$$

On the other hand, several years ago Radke and Prausnitz[4] proposed a prediction method by which we could calculate multi-solute adsorption equilibrium using each single-solute adsorption isotherms. Further recently Jossens and Prausnitz et al.[1] modified Radke's method and at present modified Radke's method can be thought to be the most reliable prediction method. So modified Radke's method is selected here for the comparison with the proposed method.

Jossens et al. thought that the fault of Radke's method was that it was difficult to obtain

the exact adsorption isotherm of single-solute system in the lower concentration range and the error of the extrapolation of the isotherm to the lower concentration range affected remarkably to the prediction results of multi-solute adsorption equilibrium. Then they proposed the Toth equation (Equation(2-30)) and another equation derived by themselves as the mathematical representation of single-solute adsorption isotherm (Equation(2-31)) instead of Newton's equation proposed by Radke et al.[4], because these two equations satisfy Henry's law at very low concentration, and are relatively simple mathematical equation, and further represent accurately relatively many single-solute isotherms. However, modified Radke's method is the same as Radke's method except the representation of single-solute adsorption isotherm. The following is the brief explanation of Toth and Jossens equation.

Toth equation[7]

Toth introduced a dimensionless quantity ψ defined by Equation(2-28),

$$\psi = \frac{d\ln C}{d\ln Q} - 1 \qquad (2\text{-}28)$$

and by examining gaseous adsorption data on heterogeneous surfaces, he found that the typical experimental results obey a function represented by Equation(2-29).

$$\psi = \lambda C^{\mu} \qquad (2\text{-}29)$$

where λ and μ are constants. Further he found that for the Langmuir equation, $\mu = 1$ in Equation(2-29) and for the Freundlich equation, $\mu = 0$. When we set $\lambda = 1/\beta$ and $\mu = \gamma$, the integration of Equation(2-28) gives the Toth equation, Equation(2-30).

$$Q = \alpha C(\beta + C^{\gamma})^{-1/\gamma} \qquad (2\text{-}30)$$

In that integration Toth used the boundary condition, $Q \to \alpha$ when $C \to \infty$.

Jossens equation[1)]

On the other hand, Jossens et al. derived Equation(2-31).

$$C = (Q/\alpha)\exp(\beta Q^{\gamma}) \qquad (2\text{-}31)$$

They thought that activated carbon is characterized by a highly heterogeneous surface. The highest energy sites are filled first so that the heat of adsorption declines rapidly with the increased surface coverage. So they assumed that the iso-

steric heat of adsorption has the form of Equation (2-32).

$$q_{st} - q'_{st} = -\lambda Q^{\gamma} \qquad (2\text{-}32)$$

where $0 < \gamma < 1$ and q'_{st} is the isosteric heat for the solute at the limit of zero surface coverage. They proposed Equation(2-33) which was corresponding to Equation(2-32) from thermodynamics.

$$\ln C = \ln Q - \ln\alpha + \beta Q^{\gamma} \qquad (2\text{-}33)$$

where γ is a constant, α and β are functions of temperature only. λ and q'_{st} in Equation(2-32) are

$$\lambda = -RT^2 \frac{d\beta}{dT_a} \qquad (2\text{-}34)$$

$$q'_{st} = -RT^2 \frac{d\ln\alpha}{dT_a} \qquad (2\text{-}35)$$

Equation(2-33) equals Equation(2-31).

Both Toth and Jossens equations have three parameters, and the parameters are determined from the single-solute adsorption equilibrium data. The procedure of prediction of multi-solute adsorption equilibrium by using the determined parameters, will be mentioned later.

The three parameters, α, β and γ of the Toth and Jossens equations were searched by SIMPLEX method

using Equation(2-27) as the performance index.

Table 2-2 shows the values of parameters in Equation(2-8), the Toth equation and Jossens equation, which were determined from the single-solute data, together with the relative fitting accuracies. Q_s's for Equation(2-8) in Table 2-2 are the determined parameters for o-phenyl phenol and dodecyl benzol sulfonic acid and for the others the same as Q_s's in Table 2-1.

The fitting accuracies of Equation(2-8) are somewhat worse than the other two equations. The reason may be thought that the other two equations have three adjusting parameters, but Equation(2-8) has only two parameters. If Equation(2-8) is modified to have more parameters, the accuracy of fitting may be thought to become better. However, we dare to use a simulating formula having two parameters for simplicity of calculation.

2-5-2 Prediction for two-solute system

Now let us predict the adsorption equilibrium of two-solute system by the method which was introduced in 2-3 using the determined parameters, k_{min},

Table 2-2 Parameters and Relative Fitting Errors of Equation(2-8), the Toth Equation(Equation(2-30)) and the Jossens Equation(Equation(2-31))

Solute	Equation(2-8)				Toth equation (Equation(2-30))				Jossens equation (Equation(2-31))				Author
	k_{min}	k_{max}	Q_s	F^b(%)	α	β	γ	F^b(%)	α	β	γ	F^b(%)	
1[a]	8.15×10^{-5}	2.08×10^{2}	5.48	2.64	4.02	0.234	0.304	2.36	6.70×10^{1}	1.48	1.25	2.74	This work
2	1.03×10^{-5}	1.08×10^{4}	5.27	6.70	273.	0.168	0.0326	1.46	5.17×10^{12}	23.8	0.208	1.47	This work
3	6.21×10^{-3}	7.21×10^{2}	4.89	3.98	3.87	0.134	0.390	2.35	9.54×10^{1}	0.412	2.09	3.39	This work
1	1.07×10^{-7}	2.15×10^{2}	8.99	16.9	18.4	0.325	0.130	2.73	4.02×10^{2}	3.12	0.647	6.67	Jossens et al.[1]
2	9.65×10^{-9}	2.44×10^{4}	8.59	7.47	10.2	0.145	0.118	2.13	1.99×10^{5}	5.56	0.581	1.88	Jossens et al.
4	3.52×10^{-7}	3.40×10^{3}	8.33	7.28	11.3	0.187	0.133	3.08	6.64×10^{3}	3.40	0.719	3.69	Jossens et al.
5	1.41×10^{-5}	4.63×10^{2}	8.45	8.27	11.7	0.260	0.174	3.19	1.34×10^{3}	3.02	0.623	3.68	Jossens et al.
6	1.84×10^{-7}	7.47×10^{2}	7.11	10.1	103.	0.288	0.0658	3.17	8.85×10^{2}	3.35	0.718	6.10	Jossens et al.
7	1.53×10^{-6}	5.97×10^{5}	6.95	5.20	63.9	0.132	0.0445	1.66	1.08×10^{6}	4.37	0.809	3.54	Jossens et al.
8	1.04×10^{-4}	2.34×10^{4}	7.50	3.89	17.4	0.139	0.0876	1.25	1.58×10^{6}	6.12	0.544	1.14	Jossens et al.
9	2.02×10^{-19}	8.17×10^{5}	5.77	4.70	1.70	0.0538	0.272	2.82	4.78×10^{2}	2.09	2.90	3.88	Jossens et al.
3	1.12×10^{-5}	6.29×10^{2}	5.32	3.35	5.54	0.214	0.182	3.45	1.09×10^{3}	3.97	0.742	3.73	Radke et al.[4]
4	8.41×10^{-6}	1.68×10^{3}	5.46	4.16	10.1	0.183	0.106	2.79	2.04×10^{3}	3.72	0.824	2.76	Radke et al.
10	2.03×10^{-14}	1.61×10^{0}	6.72	19.6	14.4	1.52	0.205	6.23	6.79×10^{-1}	3.16	0.469	7.34	Radke et al.
11	4.66×10^{-11}	9.35×10^{-1}	6.91	19.2	100.	2.02	0.171	3.48	7.28×10^{0}	5.02	0.138	5.69	Radke et al.

a See Table 2-1.

b $F = \left[\sum_{i=1}^{N} \{(Q_{icalc} - Q_{iexp})/Q_{iexp}\}^2/N\right]^{1/2}$, N : No. of experimental points

k_{max} and Q_s in Table 2-2. When an arbitrary set of concentration at adsorption equilibrium, C_1 and C_2, is given, the amounts of adsorption for each solutes, Q_1 and Q_2, can be obtained by Equation(2-26).

$$Q_i(C_i) = \frac{Q_{si}C_i}{\ln(k_{i,max}/k_{i,min})} \int_{k_{i,min}}^{k_{i,max}} \frac{dk_i^*}{1+\sum_{j=1}^{n} (k_i^*/k_{i,max})^{K_{ij}} k_{j,max}C_j} \qquad (2\text{-}26)$$

where

$$K_{ij} = \ln(k_{j,max}/k_{j,min})/\ln(k_{i,max}/k_{i,min}) \qquad (2\text{-}25)$$

The prediction results obtained as mentioned above for phenol - p-nitrophenol and p-cresol - p-nitrophenol systems are shown by solid lines in Figure 2-3 to 2-6.

Next the prediction of multi-solute adsorption equilibrium is performed by two modified Radke's method[1] in which the Toth and the Jossens equations are used respectively.

Radke et al.[4] applied the thermodynamics of ideal dilute solutions toward establishing a method for predicting multi-solute adsorption. The following equations, which were used to predict the multi-

solute equilibrium, were derived by them.

Equation(2-36) represents the spreading pressure in adsorbed phase for single-solute system.

$$\pi(C_i^\circ) = \frac{RT_a}{S} \int_0^{C_i^\circ} \{Q_i^\circ(C_i^\circ)/C_i^\circ\} dC_i^\circ \qquad (2\text{-}36)$$

By assuming the ideal adsorbed phase,

$$1/Q_T = \sum_{i=1}^{n} (z_i/Q_i^\circ) \qquad (2\text{-}37)$$

From the phase equilibria,

$$C_i = C_i^\circ(\pi) z_i \qquad (2\text{-}38)$$

From the definition of z,

$$\sum_{i=1}^{n} z_i = 1 \qquad (2\text{-}39)$$

And Equation(2-40) is held in the adsorbed phase when the adsorption equilibrium is achieved in multi-solute system.

$$\pi_1 = \pi_2 = \cdots = \pi_i = \cdots = \pi_n = \pi \qquad (2\text{-}40)$$

Practically the multi-solute adsorption equilibrium can be predicted by Radke's method using the Toth and Jossens equation[1] (that is, modified Radke's method) in the following way. For simplicity the procedure is illustrated below for two-solute equilibrium.

When C_1 and C_2 are given, by giving the appropriate value for z_1, we can obtain z_2 by Equation(2-39), $C_1^\circ(\pi)$ and $C_2^\circ(\pi)$ by Equation(2-38) and $S\pi_1/RT_a$ and $S\pi_2/RT_a$ by Equation(2-36) and the Toth or Jossens equation. By searching the value of z_1 so as to satisfy Equation(2-40) (that is, $S\pi_1/RT_a = S\pi_2/RT_a$), we can calculate Q_T by Equation(2-37) and $Q_T z_1$ and $Q_T z_2$ are the amounts of adsorption for each solutes.

Using the parameters α, β and γ in Table 2-2, the two-solute adsorption equilibria were predicted by two Radke's method mentioned above for the systems introduced in 2-4, and the results are also shown in Figures 2-3 to 2-6 by broken lines and chain lines with one dot.

Further for eight two-solute systems by Jossens et al.[1] and Radke et al.[4] the results, which were predicted by two modified Radke's methods and the proposed method, are represented in Figures 2-7 to 2-22 together with the experimental data. Then the accuracies by the three prediction methods are shown in Table 2-3 for all two-solute systems introduced here. The underlines in Table 2-3 tell us which method gives us the best result for each system.

Table 2-3 Comparison of Prediction Accuracy of Three Method for Two-Solute Adsorption Equilibrium

Solute	T	Activated carbon	No. of exp. points	Av. relative difference F[c]			Prediction errors		Author
				This work	R(T)[d]	R(J)[e]	A	B	
1[a](A)[b]/2(B)	35	CAL	21	0.235	<u>0.204</u>	0.223	+[f]	-[f]	This work
3(A)/2(B)	35	CAL	16	<u>0.166</u>	0.265	0.517	-	+	This work
2(A)/1(B)	20	B10-I	230	0.150	0.101	<u>0.095</u>	good	good	Jossens et al.[1]
2(A)/4(B)	20	B10-I	64	0.158	<u>0.109</u>	0.111	good	good	Jossens et al.
2(A)/5(B)	20	B10-I	64	<u>0.251</u>	0.357	0.342	+	-	Jossens et al.
4(A)/6(B)	20	B10-I	64	<u>0.179</u>	0.185	0.214	+	-	Jossens et al.
7(A)/2(B)	20	B10-I	45	0.265	0.307	<u>0.125</u>	+	-	Jossens et al.
8(A)/9(B)	20	B10-II	16	<u>0.224</u>	0.784	0.780	+	-	Jossens et al.
4(A)/3(B)	25	Filtrasorb 300	29	<u>0.102</u>	0.220	0.119	good	good	Radke et al.[4]
10(A)/11(B)	25	Filtrasorb 300	19	0.149	<u>0.043</u>	0.055	good	good	Radke et al.

a See Table 2-1.

b Solute A is more adsorbable than Solute B.

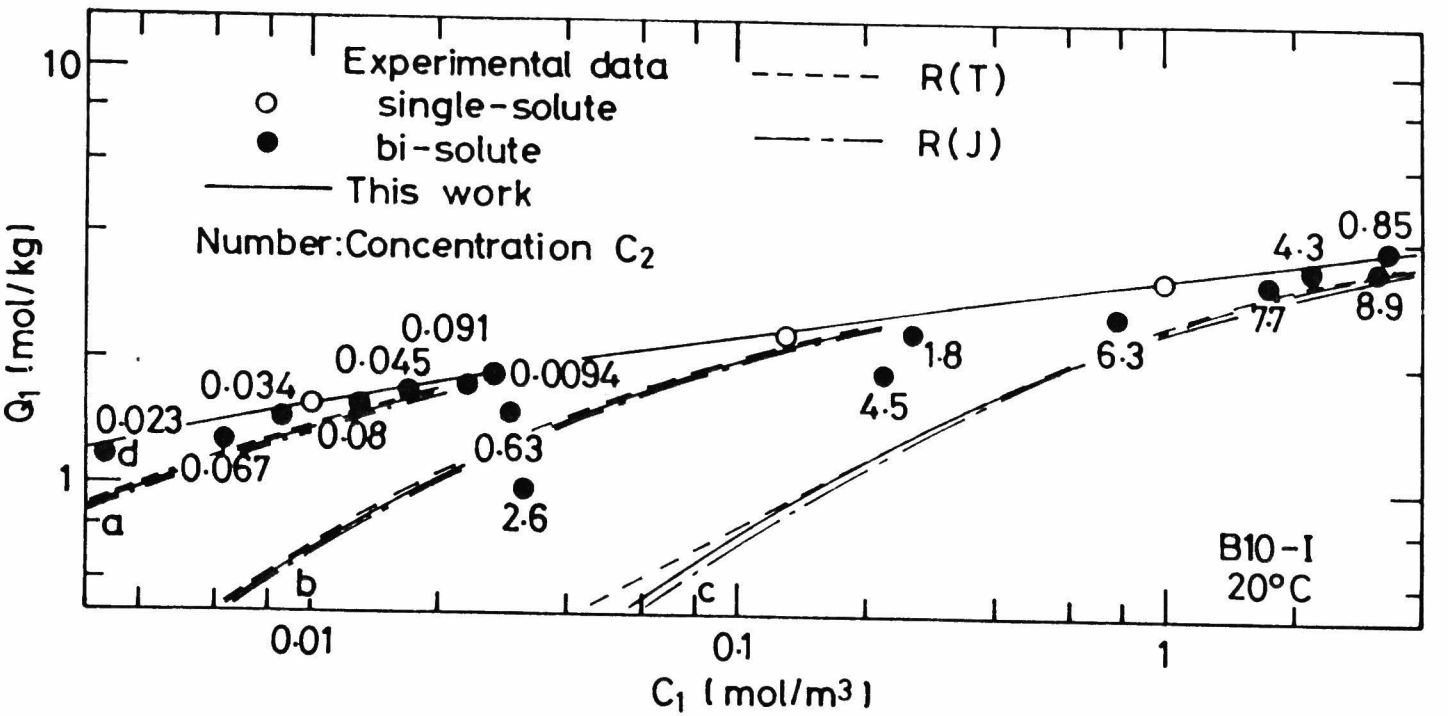
c $F = (1/2N) \sum_{i=1}^{N} (|Q_{1i,calc} - Q_{1i,exp}|/Q_{1i,exp} + |Q_{2i,calc} - Q_{2i,exp}|/Q_{2i,exp})$

N : No. of experimental points, 1,2 : Solute

d Modified Radke's method in which the Toth equation was adopted

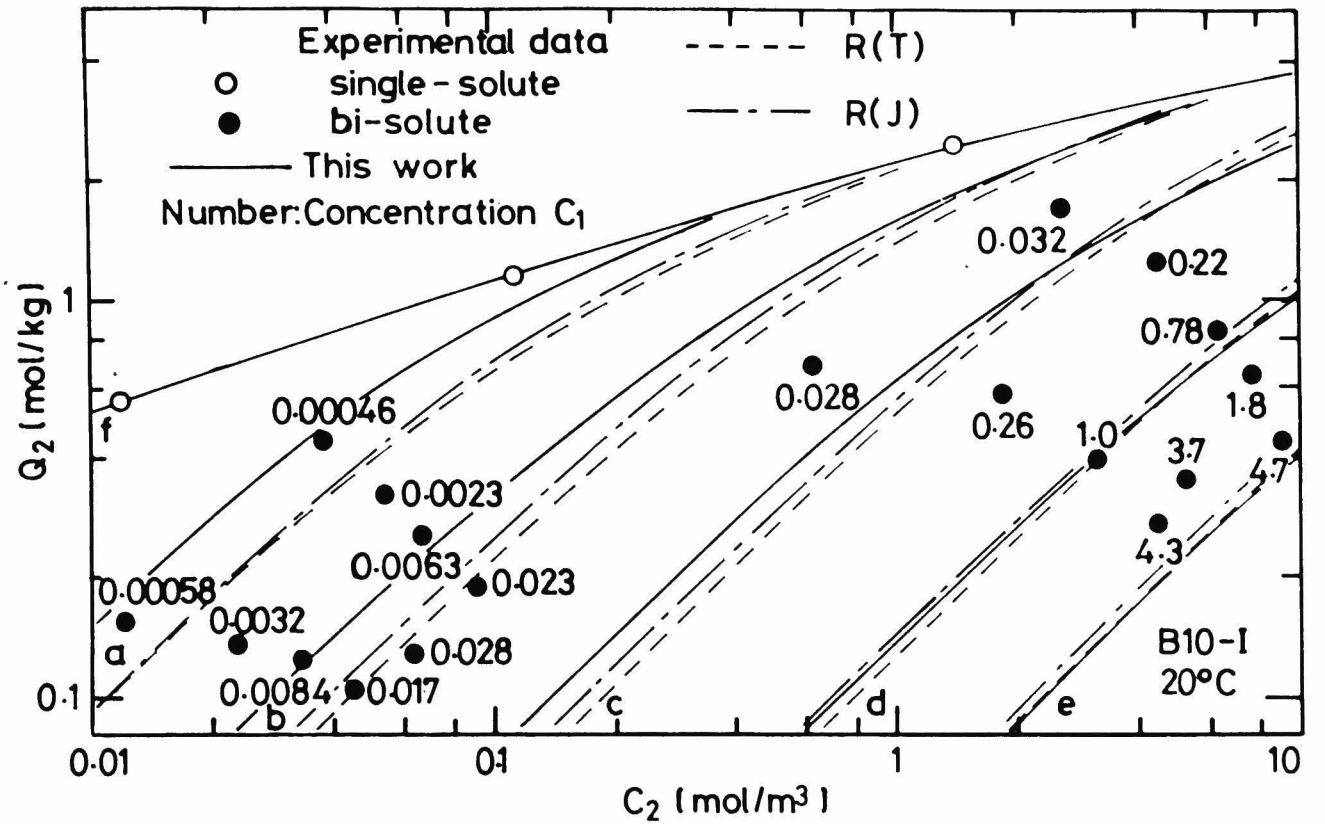
e Modified Radke's method in which the Jossens equation was adopted

f + : overprediction, - : underprediction



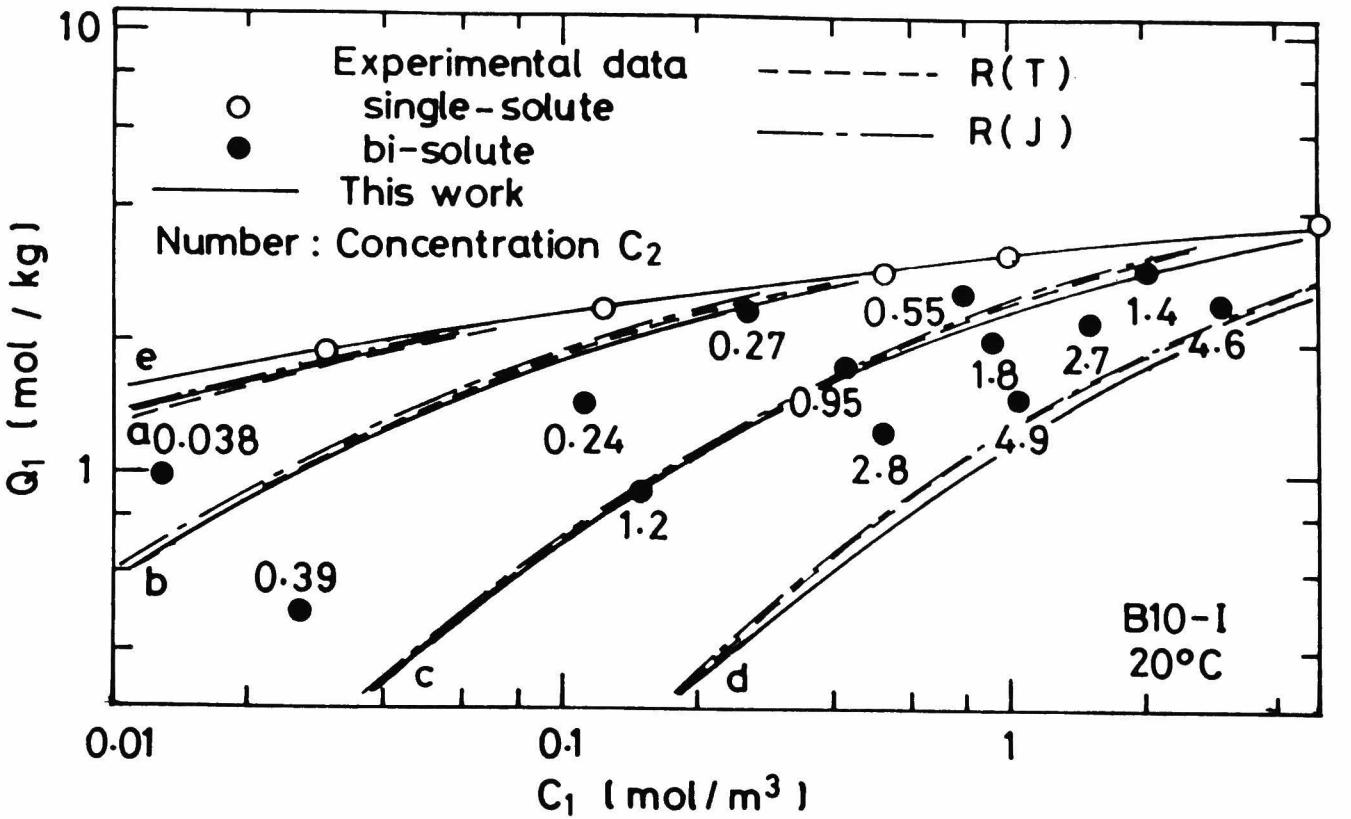
(a)C_2=0.1, (b)C_2=1.0, (c)C_2=10.0, (d)C_2=0.0[mol/m^3]

Fig.2-7 Adsorption isotherms of p-nitrophenol(1) in the presence of phenol(2)



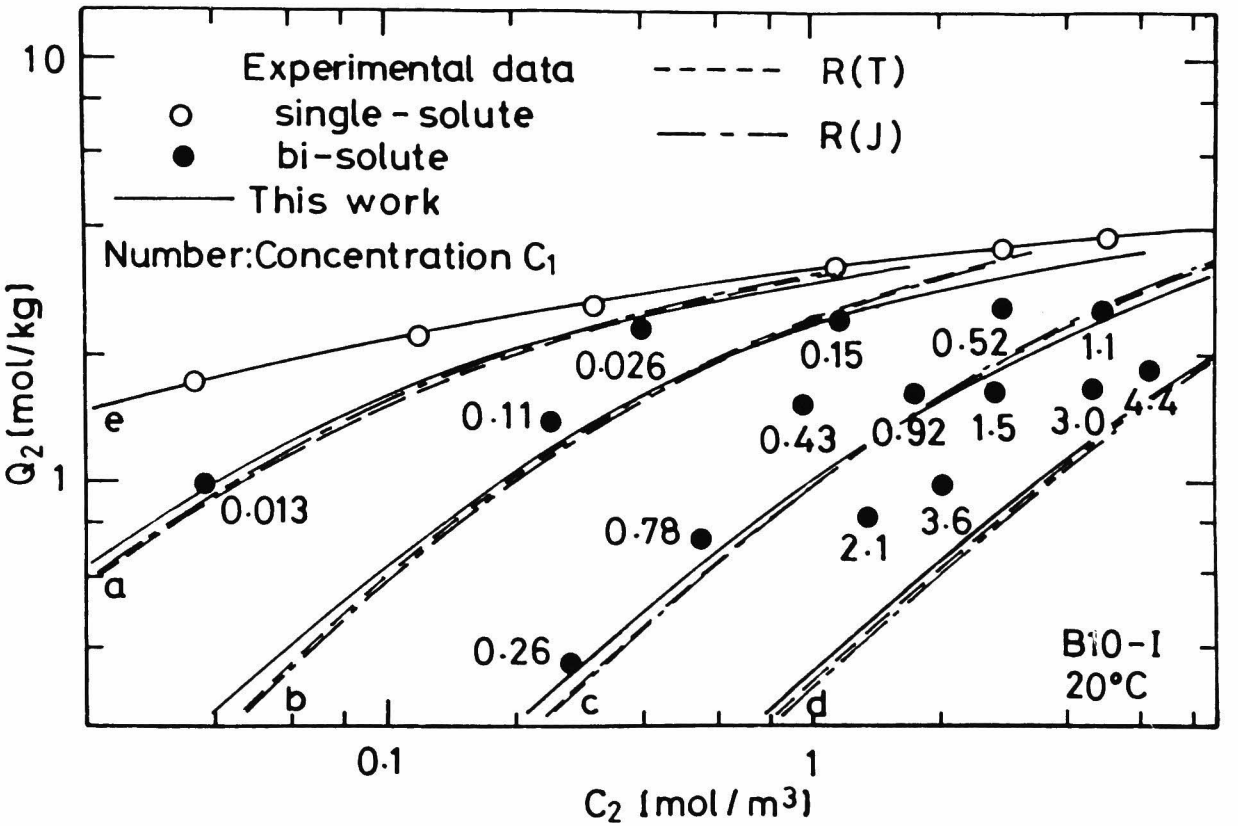
(a)C_1=0.001, (b)C_1=0.01, (c)C_1=0.1, (d)C_1=1.0, (e)C_1=5.0, (f)C_1=0.0[mol/m^3]

Fig.2-8 Adsorption isotherms of phenol(2) in the presence of p-nitrophenol(1)



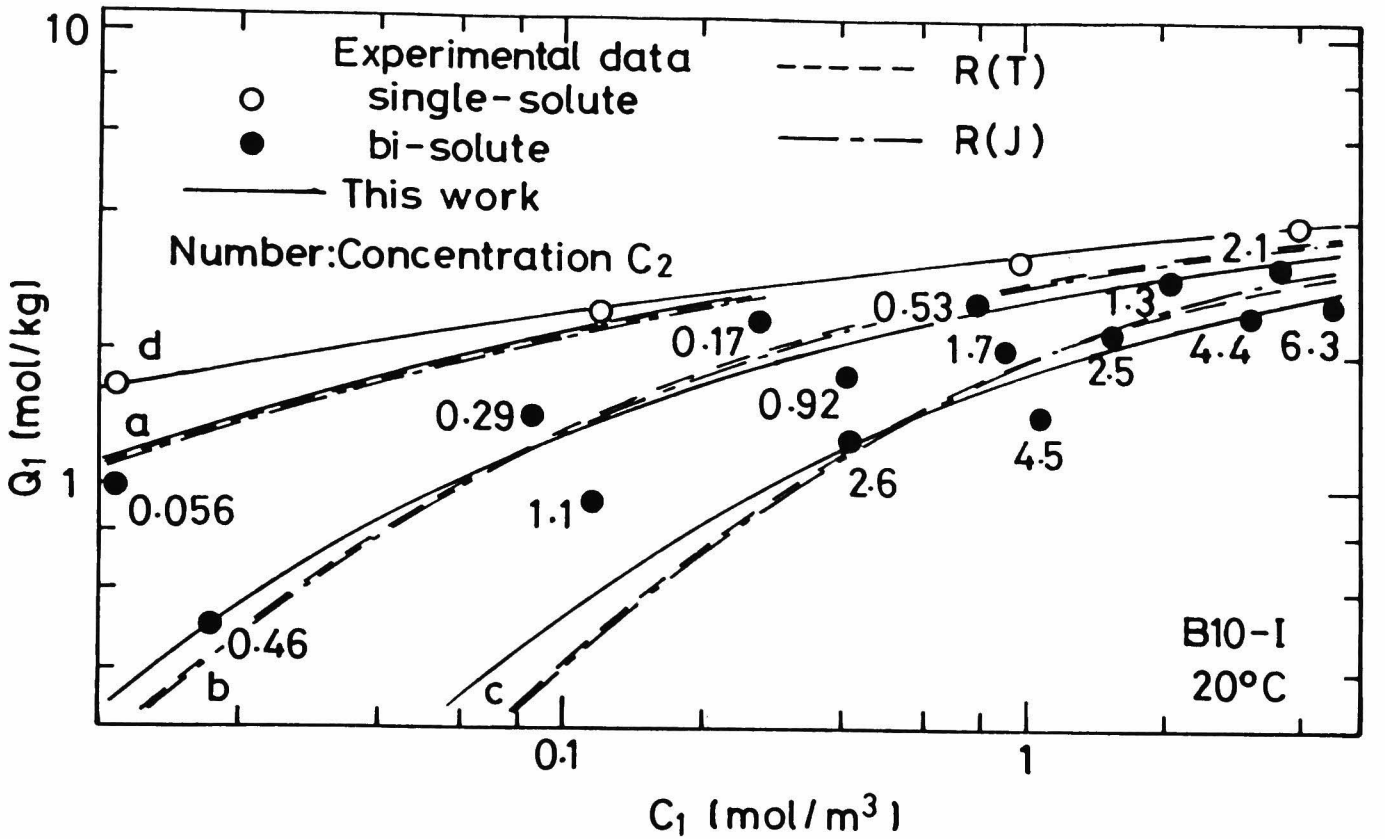
(a)C_2=0.01, (b)C_2=0.1, (c)C_2=1.0, (d)C_2=5.0, (e)C_2=0.0[mol/m^3]

Fig.2-9 Adsorption isotherms of p-nitrophenol(1) in the presence of p-chlorophenol(2)



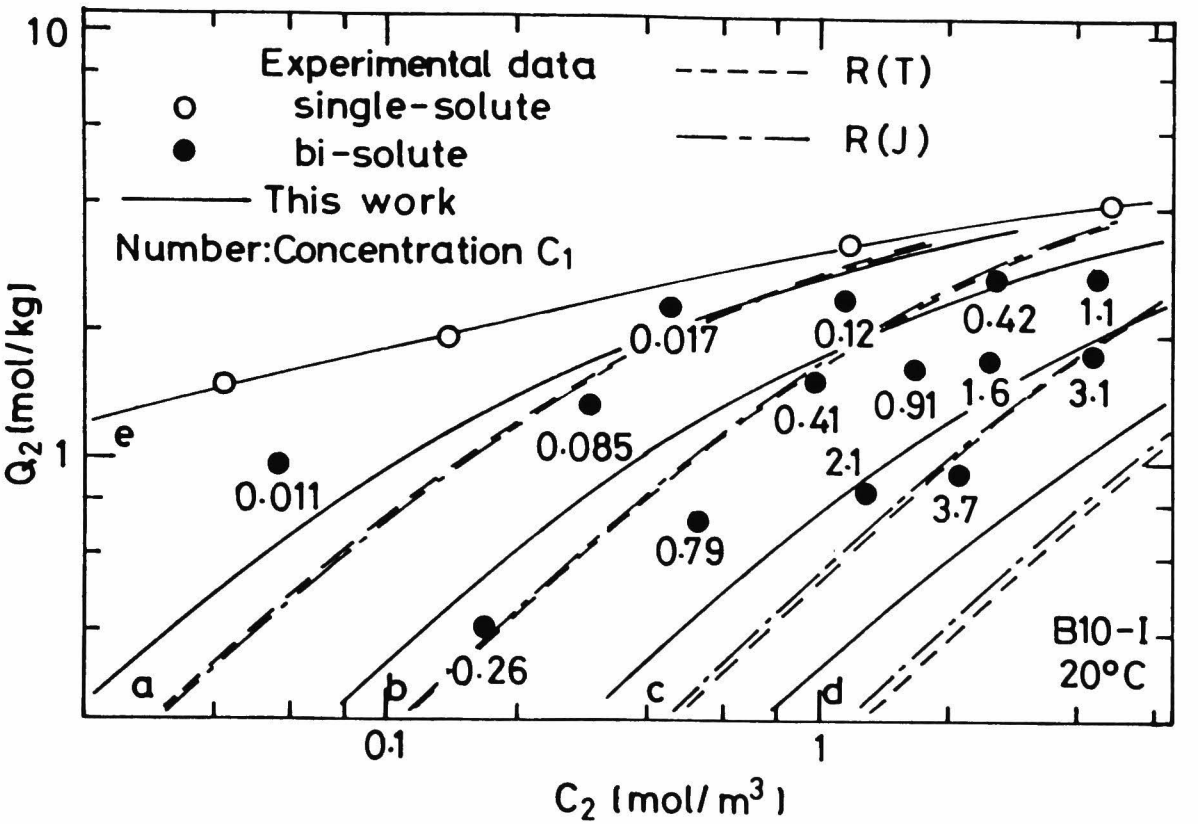
(a)C_1=0.01, (b)C_1=0.1, (c)C_1=1.0, (d)C_1=5.0, (e)C_1=0.0[mol/m^3]

Fig.2-10 Adsorption isotherms of p-chlorophenol(2) in the presence of p-nitrophenol(1)



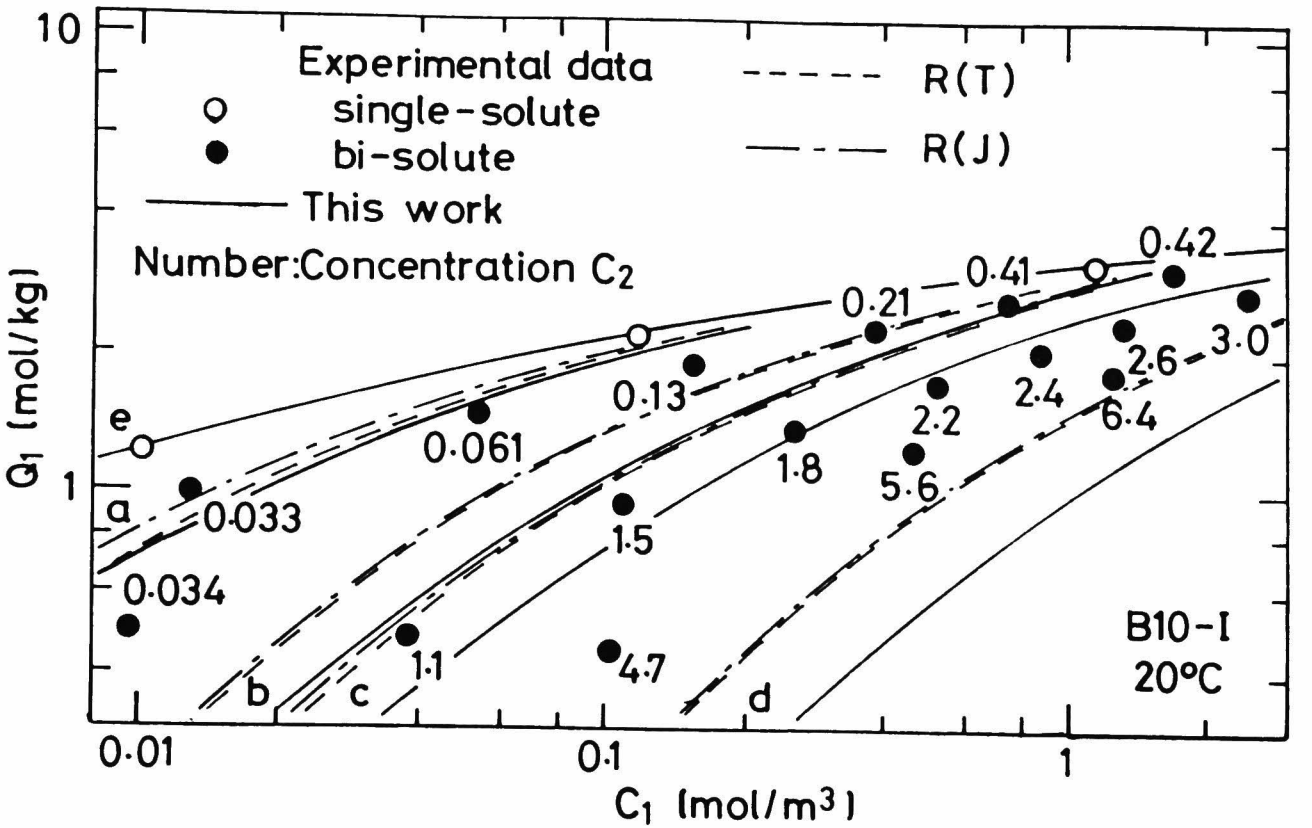
(a)C_2=0.1, (b)C_2=1.0, (c)C_2=5.0, (d)C_2=0.0[mol/m^3]

Fig.2-11 Adsorption isotherms of p-nitrophenol(1) in the presence of benzoic acid(2)



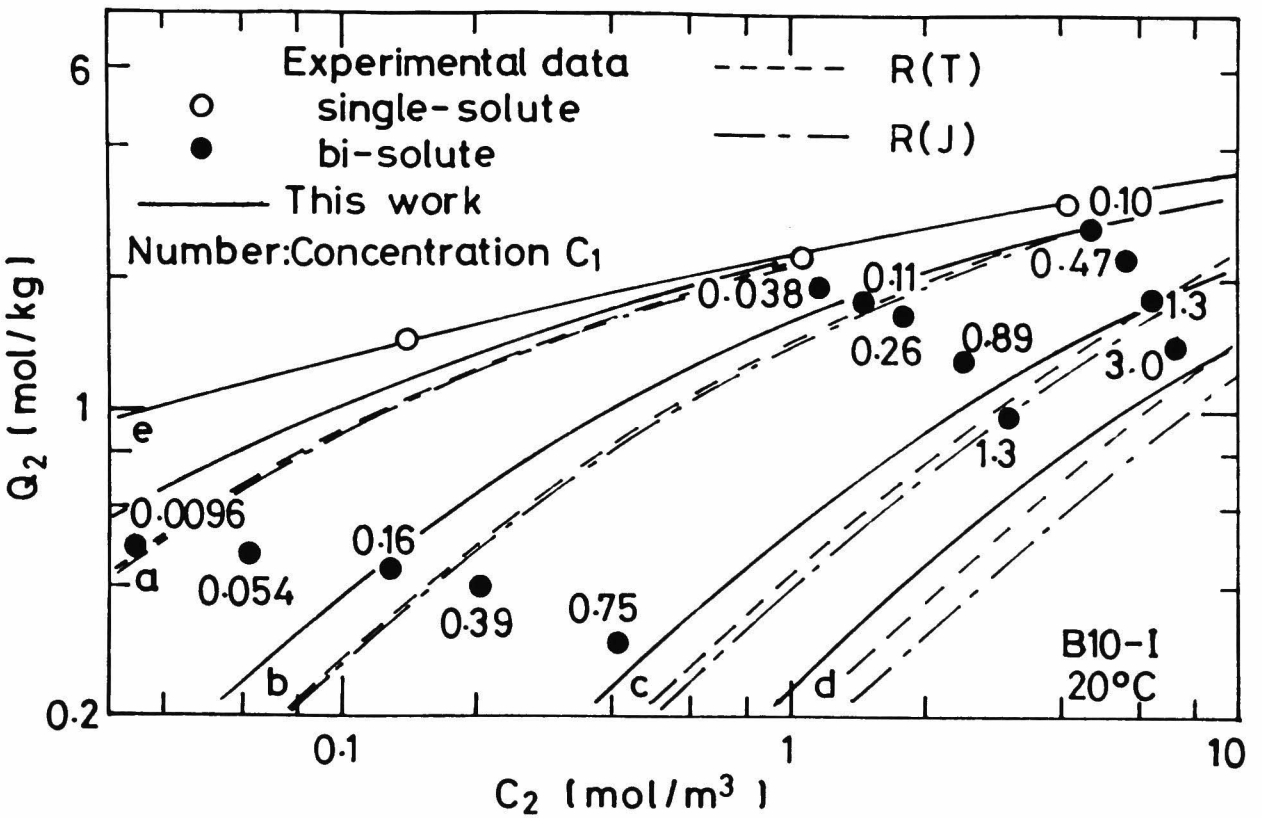
(a)C_1=0.01, (b)C_1=0.1, (c)C_1=1.0, (d)C_1=5.0, (e)C_1=0.0[mol/m^3]

Fig.2-12 Adsorption isotherms of benzoic acid(2) in the presence of p-nitrophenol(1)



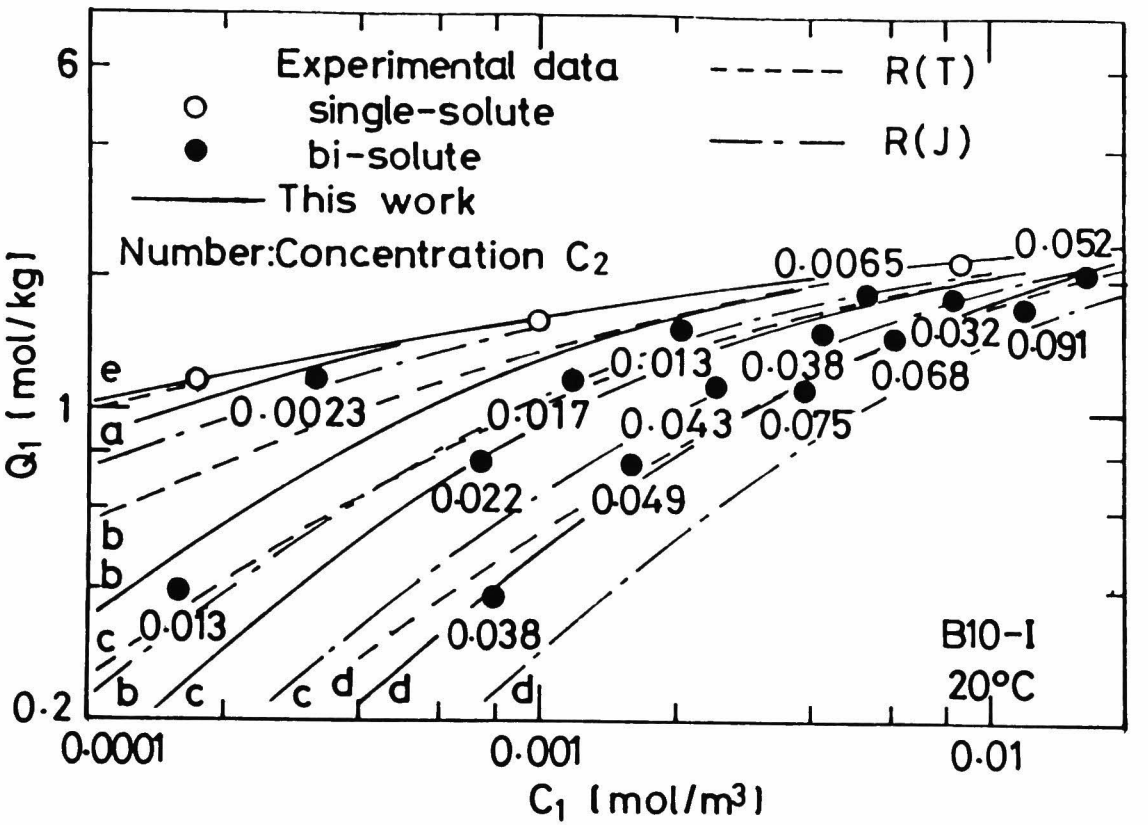
(a)C_2=0.05, (b)C_2=0.5, (c)C_2=1.0, (d)C_2=10.0, (e)C_2=0.0[mol/m^3]

Fig.2-13 Adsorption isotherms of p-chlorophenol(1) in the presence of phenyl acetic acid(2)



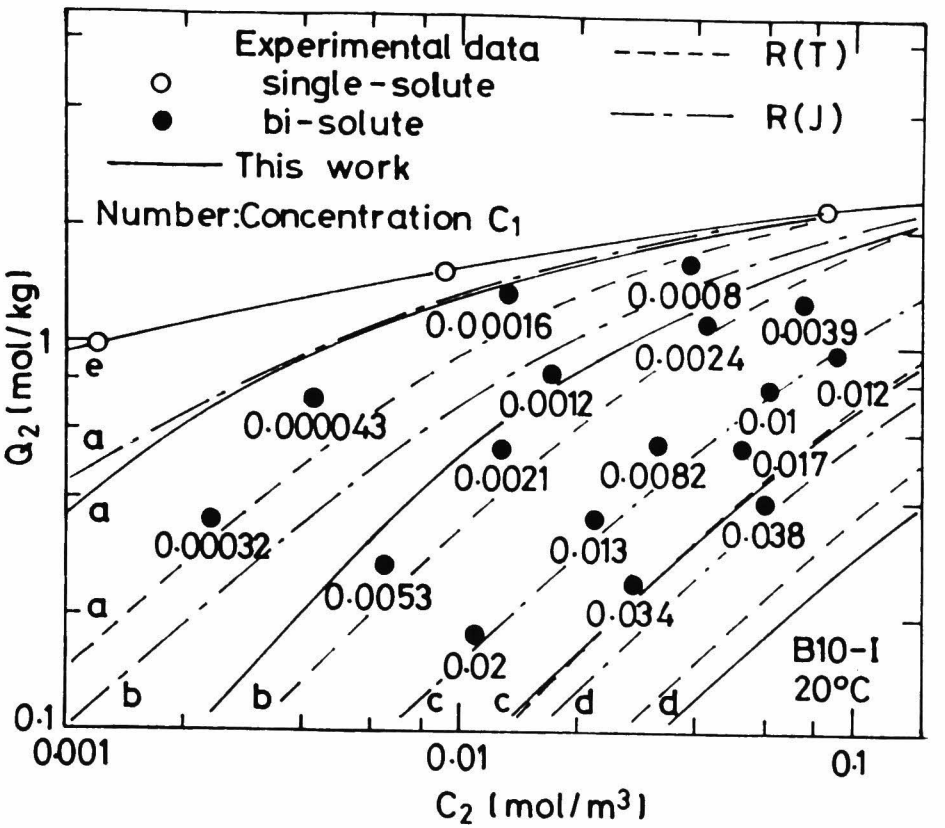
(a)C_1=0.01, (b)C_1=0.1, (c)C_1=1.0, (d)C_1=3.0, (e)C_1=0.0[mol/m^3]

Fig.2-14 Adsorption isotherms of phenyl acetic acid(2) in the presence of p-chlorophenol(1)



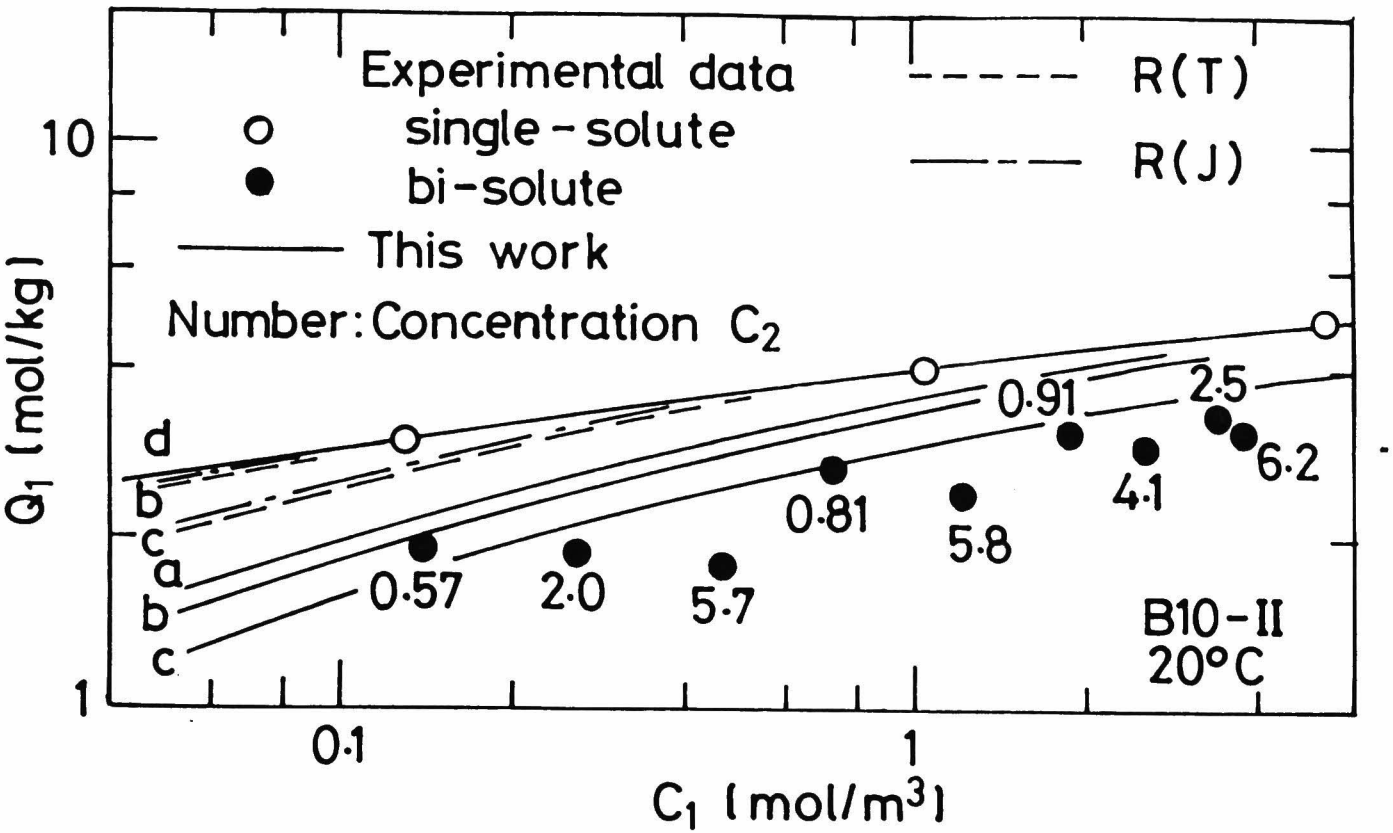
(a)C_2=0.001, (b)C_2=0.01, (c)C_2=0.03, (d)C_2=0.1, (e)C_2=0.0[mol/m^3]

Fig.2-15 Adsorption isotherms of o-phenyl phenol(1) in the presence of p-nitrophenol(2)



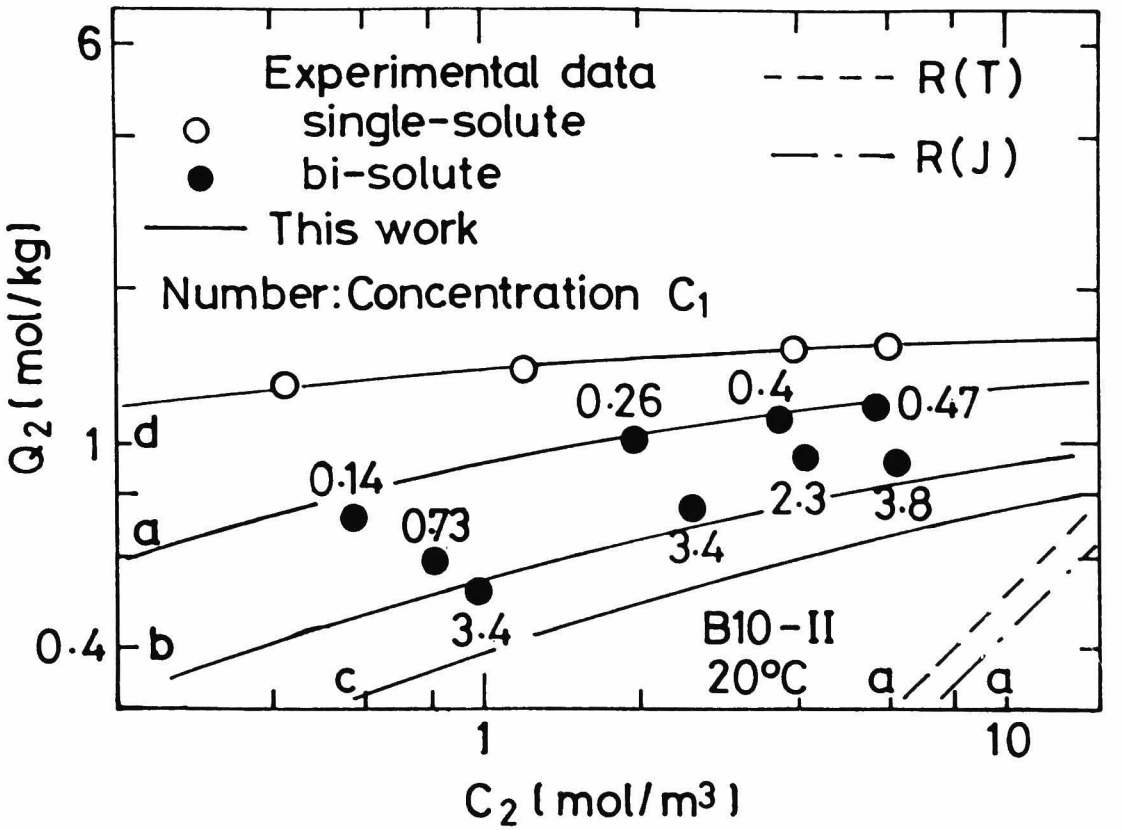
(a)C_1=0.0001, (b)C_1=0.001, (c)C_1=0.01, (d)C_1=0.03, (e)C_1=0.0[mol/m^3]

Fig.2-16 Adsorption isotherms of p-nitrophenol(2) in the presence of o-phenyl phenol(1)



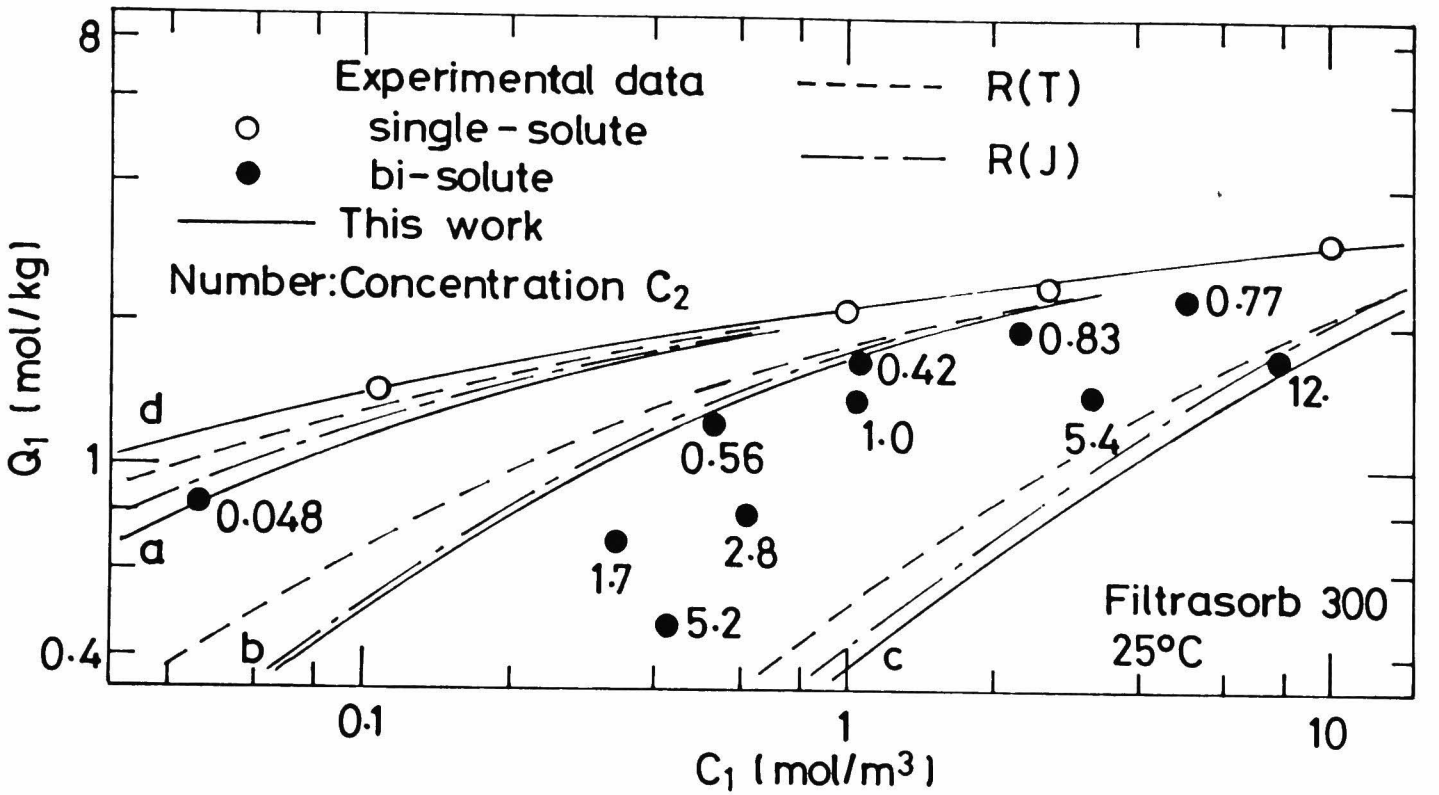
(a)C_2=0.5, (b)C_2=1.0, (c)C_2=5.0, (d)C_2=0.0[mol/m^3]

Fig.2-17 Adsorption isotherms of 2,4-dichlorophenol(1) in the presence of dodecyl benzol sulfonic acid(2)



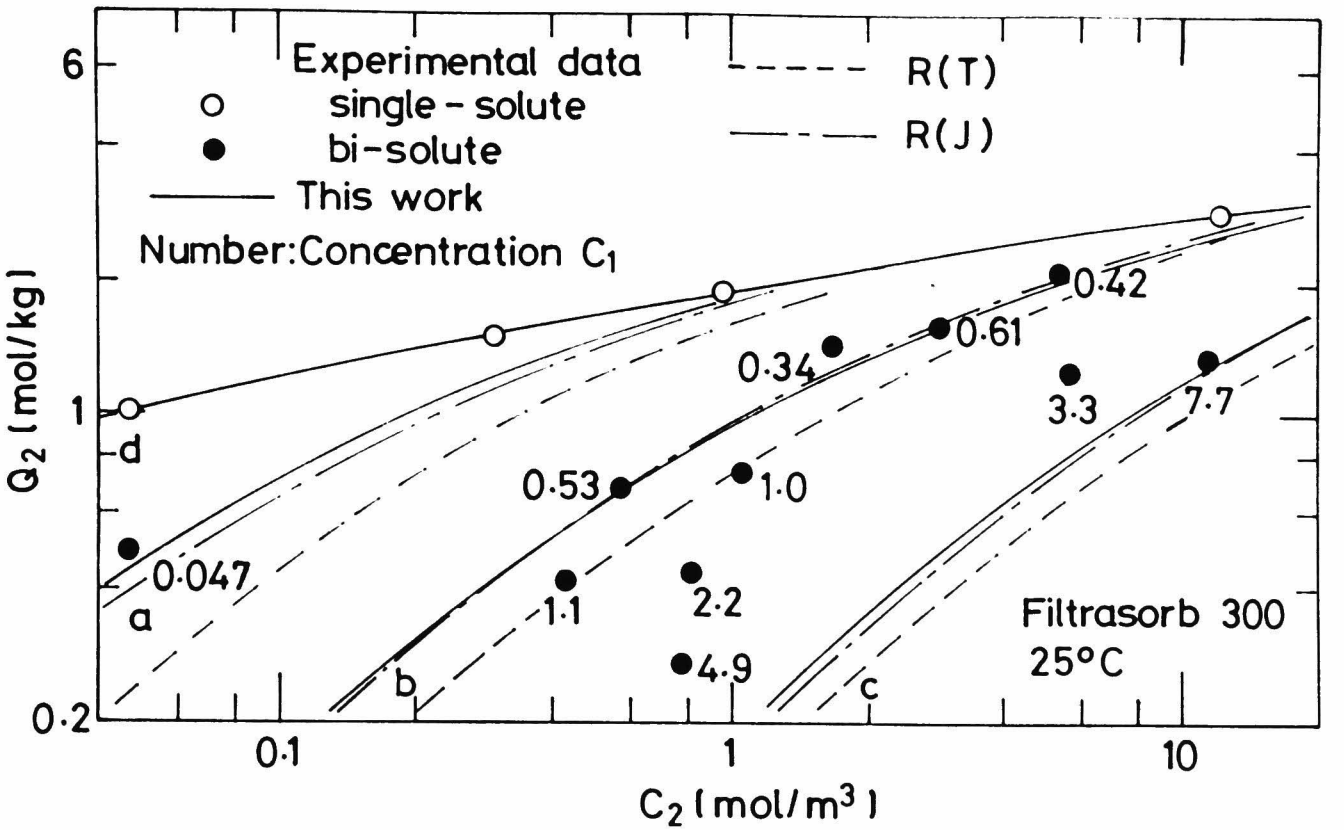
(a)C_1=0.1, (b)C_1=1.0, (c)C_1=3.0, (d)C_1=0.0[mol/m^3]

Fig.2-18 Adsorption isotherms of dodecyl benzol sulfonic acid(2) in the presence of 2,4-dichlorophenol(1)



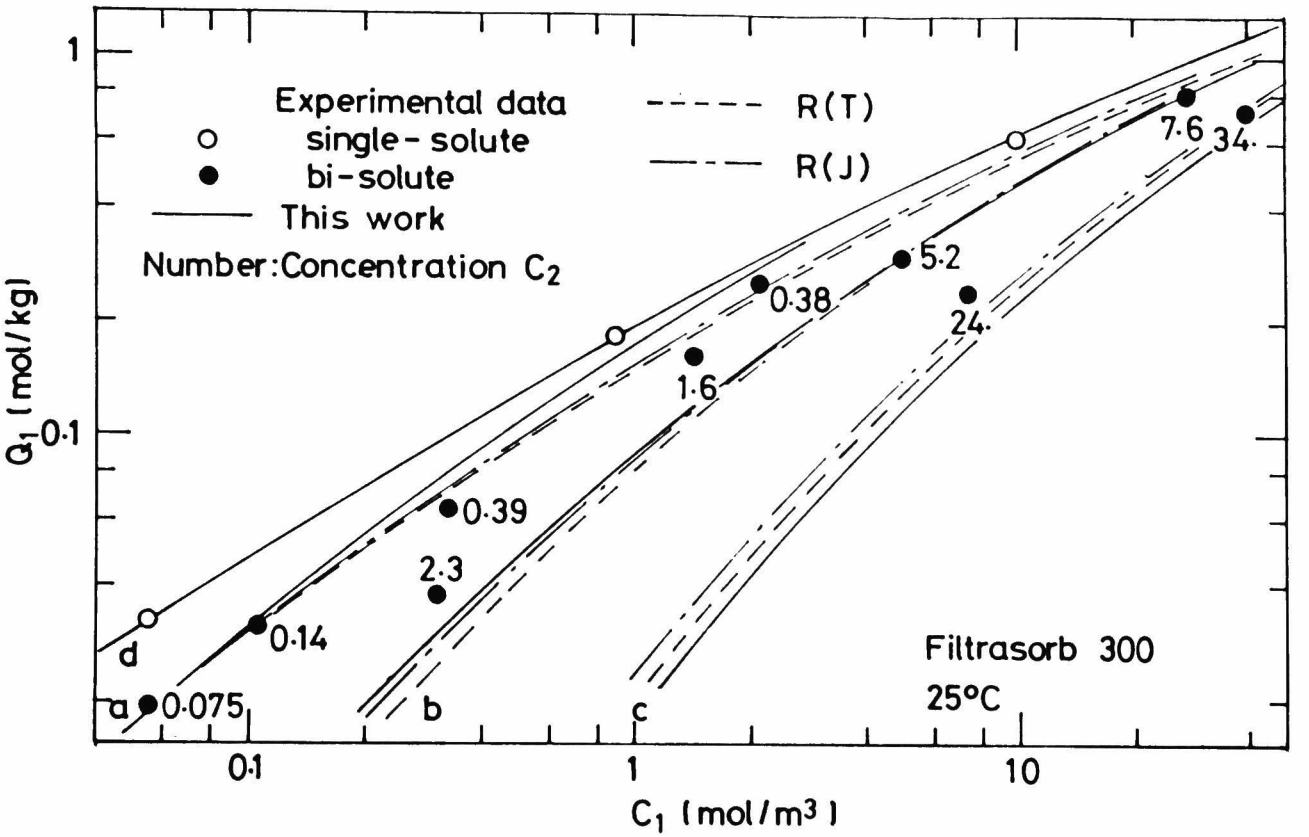
(a)C_2=0.048, (b)C_2=0.56, (c)C_2=12.0, (d)C_2=0.0[mol/m^3]

Fig.2-19 Adsorption isotherms of p-chlorophenol(1) in the presence of p-cresol(2)



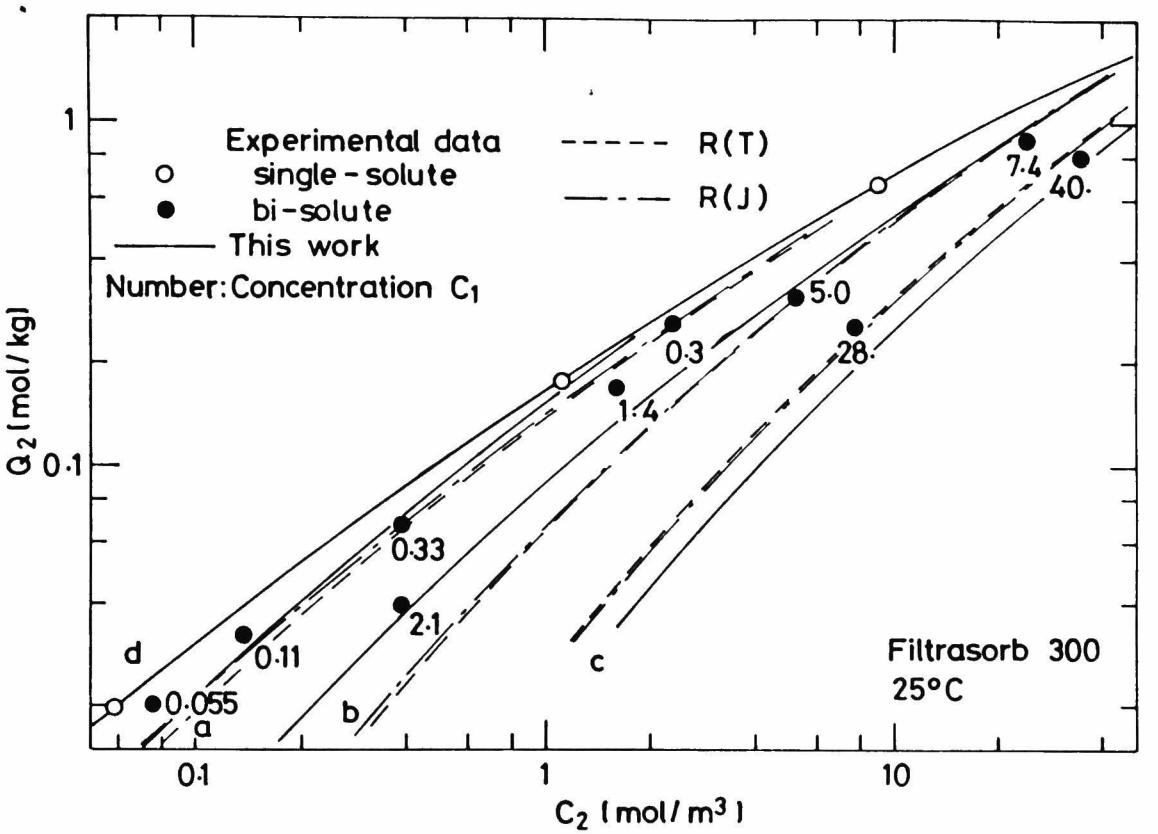
(a)C_1=0.047, (b)C_1=0.53, (c)C_1=7.7, (d)C_1=0.0[mol/m^3]

Fig.2-20 Adsorption isotherms of p-cresol(2) in the presence of p-chlorophenol(1)



(a)C_2=0.14, (b)C_2=5.2, (c)C_2=34.0, (d)C_2=0.0[mol/m^3]

Fig.2-21 Adsorption isotherms of acetone(1) in the presence of propionitrile(2)



(a)C_1=0.30, (b)C_1=5.0, (c)C_1=40.0, (d)C_1=0.0[mol/m^3]

Fig.2-22 Adsorption isotherms of propionitrile(2) in the presence of acetone(1)

And we can find that the proposed method has more stable accuracy than the others and that there is no system with especially wrong result in the proposed method, in spite of a little insufficiency of the fitting for single-solute equilibrium.

Further from the first, eighth and ninth columns of Table 2-3, we should notice that the more adsorbable solutes for single-solute system in the solutes involved in the two-solute systems, are always predicted higher than experimental values for two-solute systems, and the less adsorbable solutes are reverse, except for one system, p-cresol - p-nitrophenol. For example, the first line of Table 2-3 shows that phenol is the more adsorbable solute for single-solute system, and its amount of adsorption for the two-solute system is overpredicted, while p-nitrophenol is underpredicted. Because the adsorption isotherms for single-solute systems, which were determined from experimental data, are not much accurate as shown in Table 2-2, the prediction results for multi-solute systems are thought to have some errors. Therefore when the isotherm of single-solute system can describe more exactly, the prediction accuracy of multi-solute system will become better.

However, if the tendency of the deviation can be observed in the prediction results as stated above after the improvement of isotherm of single-solute system, the reason may be as follows. That is, although the more adsorbable solute occupies the wider portion on the adsorbent surface, the affinity among adsorbate molecules for different species is stronger than for same species, so the less adsorbable solute might be enhanced. So the more adsorbable solute is overpredicted by the proposed model, while the less adsorbable solute is underpredicted. Hence the present model has a possibility of improvement of exactitude by taking into account of the effect of the interaction among adsorbate molecules, and this is just a problem awaiting solution in future.

2-6 Conclusions

1. Recently to predict multi-solute adsorption equilibrium by using of the single-solute adsorption equilibrium data, Radke et al. have proposed a method by applying the thermodynamics of ideal solution to adsorbed phase, and Jossens et al. have modified

Radke's method to obtain better prediction accuracy. Then modified Radke's method can be thought to be the most reliable prediction method at present. In this chapter, a prediction method for multi-solute equilibrium, which was on the basis of a Langmuir type adsorption equilibrium model for heterogeneous surface of adsorbent, was proposed, and its prediction accuracy was compared with two modified Radke's methods.

2. While two modified Radke's method require three parameters determined from each single-solute data, the proposed method requires only two parameters when the densities of solutes are known. Further the proposed model can be performed without trial-and-error calculation so its calculation for prediction is simpler than the others.

3. The prediction accuracy of the proposed method for ten two-solute systems was the same or a little better and more stable than two modified Radke's methods in spite of its different approach.

Appendix

When Roginsky's approximation can apply to the model or $k_{max} >> 1$ and $k_{min} << 1$, Equations(2-12) or (2-14) hold. By the derivative of Equations(2-12) or (2-14), we can get

$$CdQ/dC = RT_a f'(E') = RT_a f'\{-RT_a \ln(aC)\} \quad (2\text{-}A\text{-}1)$$

$$C^2 dQ/dC = f(k') = f(1/C) \quad (2\text{-}A\text{-}2)$$

From Equations(2-A-2) and (2-6),

$$C^2 dQ/dC = A/k' = AC \quad (2\text{-}A\text{-}3)$$

or

$$CdQ/dC = A \quad (2\text{-}A\text{-}4)$$

On the other hand, the plot of CdQ/dC vs. C, which was obtained from the experimental data of single-solute adsorption equilibria for phenol, p-nitrophenol and p-cresol mentioned in 2-4, is shown in Figure 2-A-1. The values of CdQ/dC for each solute in Figure 2-A-1 are almost independent of C, that is, f'(E') is constant in consideration of Equation(2-A-1). As the Frumkin-Temkin equation describes the adsorption isotherm in which the distribution of the adsorption sites for E is constant, Figure 2-A-1 shows that these single-solute adsorption systems obey the Frumkin-Temkin equation. Next we can find from Equation(2-A-4) that

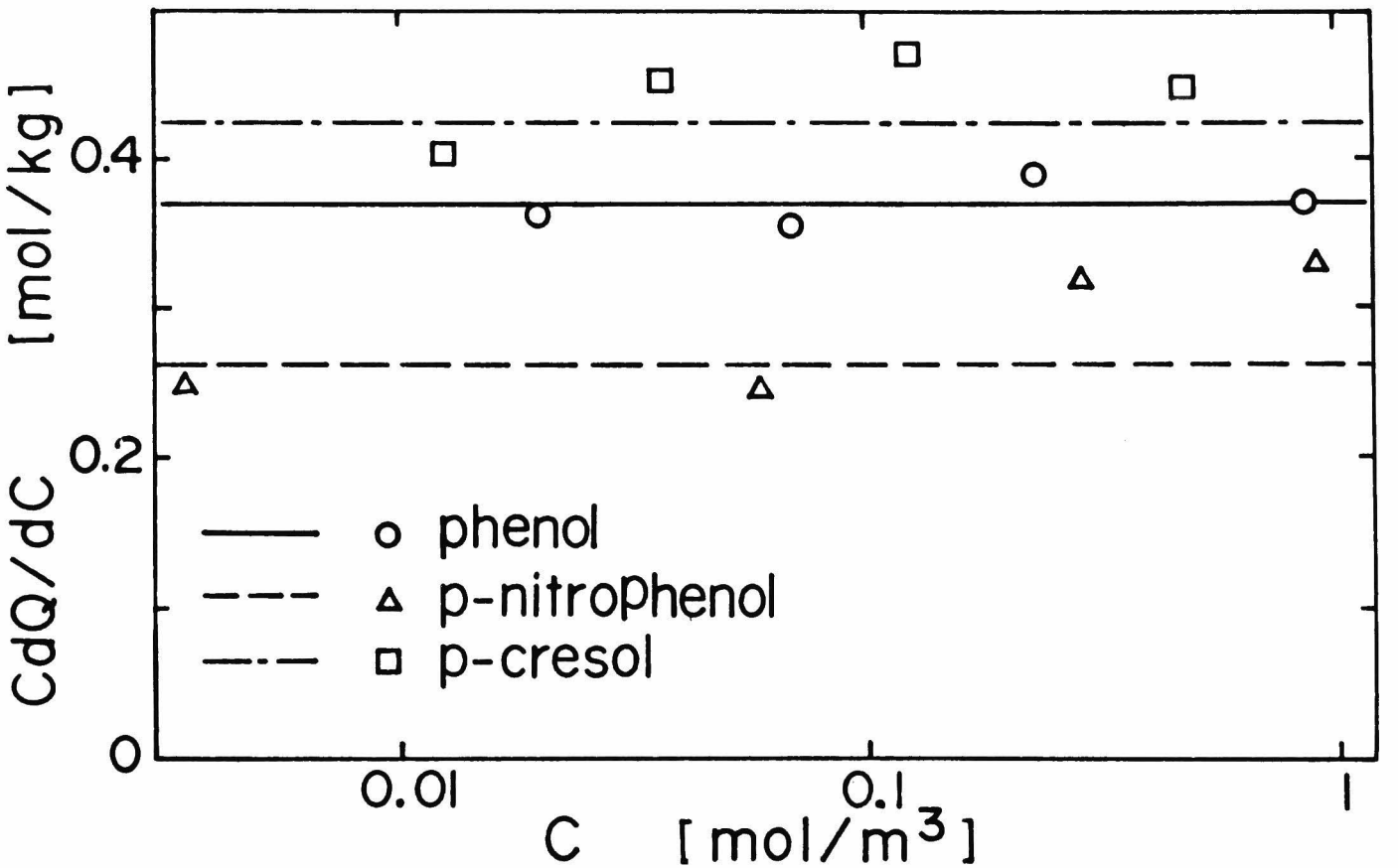


Fig.2-A-1 CdQ/dC vs. C

the value of CdQ/dC equals A. The lines in Figure 2-A-1 represent the value of A calculated by Equation (2-7) and the parameters in Table 2-2, and they agree with the experimental points. This agreement supports the reliability of the assumption of f(k) = A/k. The same results could be obtained for other single-solute systems except acetone and propionitrile by Radke et al.. Because $k_{max} >> 1$ does not hold for these two systems as shown in Table 2-2, CdQ/dC obtained from experimental data did not agree with calculated A.

From Equation(2-A-2) we can find that f(k) can be determined by the plot of C^2dQ/dC vs. 1/C, but the derivative of the experimental adsorption isotherm is very unstable and so the accurate f(k) can not be obtained directly from this plot. However, the plot of C^2dQ/dC vs. 1/C is still useful to obtain the information about the form of f(k).

For reference, the forms of the functions, f(k) and f'(E), for the adsorption systems, which obey the Frumkin-Temkin equation, the Freundlich equation and this work, are shown in Table 2-A-1.

Table 2-A-1 Relationship among f(k), f'(E) and Each Type of Adsorption Isotherm

	f(k)	f'(E)
Frumkin-Temkin eq. This work	A/k	A/RT_a = const
Freundlich eq.	$\alpha\beta k^{-\beta-1}$	$(\alpha\beta/RT_a)a^{-\beta}\exp(-\beta E/RT_a)$

where α, β are the coefficients of the Freundlich equation, $Q = \alpha C^{\beta}$.

Nomenclature

A	= coefficient of Equation(2-6)	[mol/kg]
a	= coefficient of Equation(2-9)	[m^3/mol]
C	= concentration of solution	[mol/m^3]
E	= heat of adsorption in Equation(2-9)	[J/mol]
F	= performance index	[-]
$f(k)$	= distribution function of patches	[mol^2/m^3kg]
$f'(E)$	= distribution function of patches, $= f(k)(a/RT_a)\exp(E/RT_a)$	[mol^2/kgJ]
k	= Langmuir coefficient	[m^3/mol]
M	= molecular weight	[kg/mol]
N	= number of experimental points	[-]
N_v	= Avogadro's number	[1/mol]
Q	= amount of adsorption	[mol/kg]
Q_k	= amount of adsorption on patches which have adsorption energy k	[mol/kg]
Q_s	= ultimate uptake capacity	[mol/kg]
Q_{sk}	= ultimate uptake capacity on patches which have adsorption energy k	[mol/kg]
$q(k,C)$	= amount of adsorption on patches which have adsorption energy k	[mol^2/m^3kg]
q_m	= base area of an adsorbed molecule	[m^2]
q_{st}	= isosteric heat of adsorption	[J/mol]

R = gas constant [J/Kmol]

S = surface area of adsorbent [m^2/kg]

T = temperature [°C]

T_a = absolute temperature [K]

$U(k^*)$ = accumulated number of patches [mol/kg]

z = mole fruction of adsorbed phase [-]

<Greek letters>

α, β, γ = coefficients of the Toth and Jossens equations

Toth ; α:[mol/kg], β:[$(mol/m^3)^{\gamma}$], γ:[-]

Jossens; α:[m^3/kg], β:[$(mol/kg)^{-\gamma}$], γ:[-]

θ = surface coverage [-]

λ, μ = coefficients of Equations(2-16), (2-29) and (2-32)

π = spreading pressure [J/m^2]

ρ = density [kg/m^3]

ψ = dimensionless quantity defined by Equation (2-28) [-]

<Subscripts>

calc = calculation

exp = experimental

i = component

max = maximum

min = minimum

<Superscripts>

* = equivalent

° = single-solute

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CHAPTER 3

APPROXIMATE DESCRIPTION OF MULTI-SOLUTE ADSORPTION EQUILIBRIUM IN ORGANIC AQUEOUS SOLUTION

3-1 Introduction

The use of adsorption process for municipal and industrial wastewater treatment has become more prevalent in recent years, and a number of studies have been made on the packed-bed adsorption by carbon granules[2,4,6], and most of them are concerned with the system of single or two solutes. However, the wastewater generally contains many kinds of pollutants, and in most cases the composition or the individual contaminants seem to be impossible to be identified from a practical point of view. Hence these studies can hardly be applied to the design of adsorption treatment system of wastewater, because they assume the solutes to be known. Consequently, we must bother to take the experimental data on the

characteristic breakthrough curve by a time-consuming flow test. Therefore it should be a very important and interesting target to take a new approach toward the development of design procedure for the process of wastewater adsorption treatment. In the prediction of breakthrough curve, it is required to have the information about the adsorption equilibrium of the wastewater. A new approximate description of the adsorption equilibrium of wastewater is proposed.

3-2 Derivation of the Approximate Description

3-2-1 Concept of the approximate description

A comprehensive index for representation of concentration is necessary to describe the characteristics of adsorption equilibrium of wastewater in which many unknown solutes are contained. The concentration of pollutants in wastewater is usually given in terms of TOC, BOD or COD, so the approximate description is proposed by the use of these comprehensive indexes. The correlation formulas for multi-solute adsorption equilibrium usually have several kinds of coefficients which prescribe the adsorption

characteristics of individual solute. The set of these coefficients can be considered to have one-to-one correspondence to each solute in the wastewater.

When there are numerous kinds of solutes, it might be possible to assume the wastewater to be a distributed system of solutes on the basis of this correspondence. Using a correlation formula which represents its multi-solute adsorption behavior, we can define a topological space composed of the coefficients and the probability density of the concentration as its coordinates. We can define a plane prescribing the distribution of coefficients of correlation formula in this space. When the correlation formula of adsorption equilibrium has n-kinds of coefficients which prescribe the adsorption characteristics of individual solute, we can define a (n+1)-dimensional topological space which is composed of the n-kinds of coefficients and the probability density of the concentration as its coordinates, and imagine a n-dimensional plane prescribing the distribution of the coefficients for the concentration of wastewater in this (n+1)-dimensional space. We call this plane Characteristic Distribution of the Coefficients for Liquid Concen-

tration, because, using this distribution, we can predict the adsorption equilibria at any conditions.

For example, when we adopt the Freundlich equation (Equation(3-1)) as correlation formula,

$$Q = a_F C^{b_F} \qquad (3\text{-}1)$$

solute i is corresponding to a set of coefficients, a_{Fi} and b_{Fi}. So the solute i in a wastewater occupies a point in the three-dimensional space composed of a_F, b_F and the probability density of concentration as its coordinates. Then the adsorption characteristics of the wastewater, which has many kinds of solutes, are described by a two-dimensional plane, the characteristic distribution of Freundlich coefficients for liquid concentration, as shown in Figure 3-1.

However, as mentioned later, a kind of coefficient which prescribes the adsorption characteristics is used in this chapter, so the topological space is two-dimensional and the characteristic distribution is represented by a curved line.

3-2-2 Formulation of the problem (Method I)

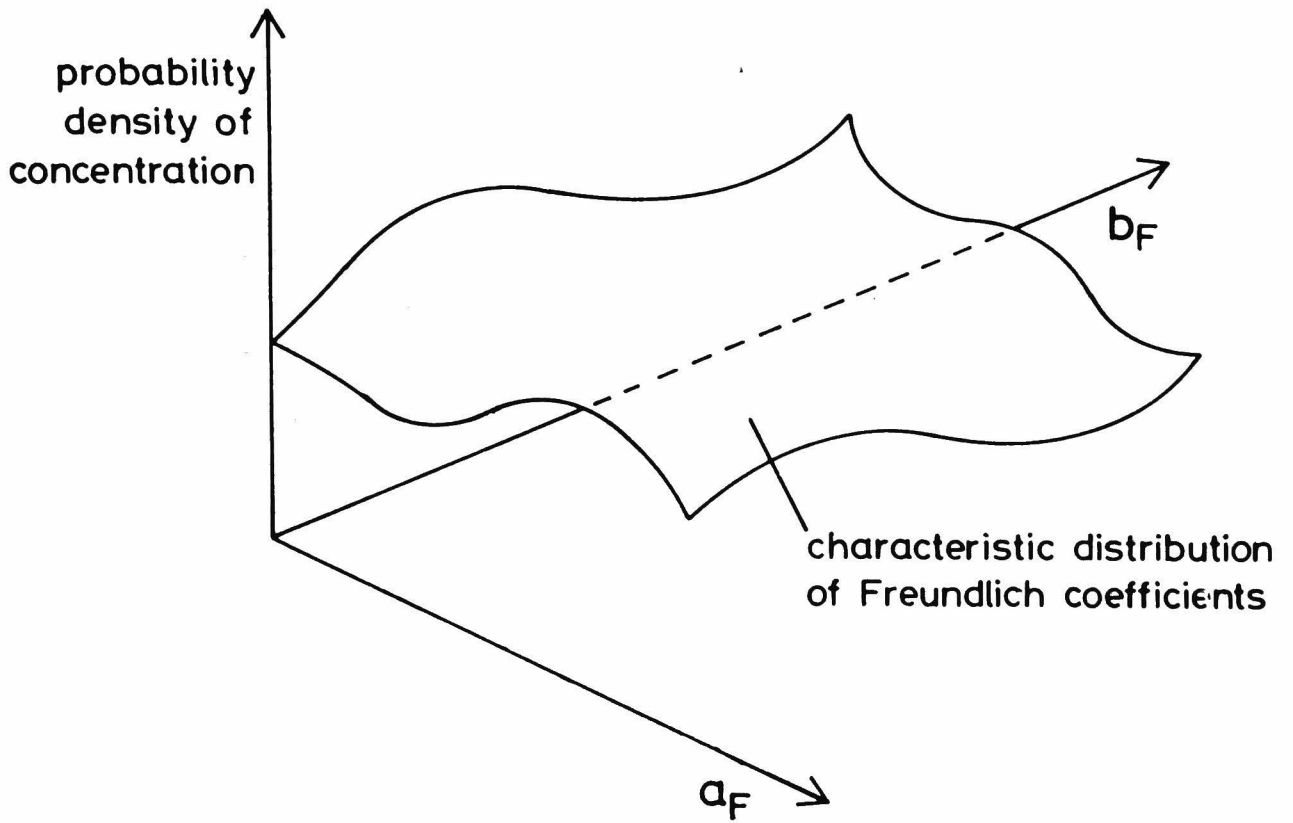

Fig.3-1 Characteristic distribution of Freundlich coefficients when Freundlich equation is adopted as correlation formula

Although there are several mathematical formulations describing multi-solute adsorption equilibria[1,3,5], the Markham-Benton equation[3], which is an extension of the Langmuir equation to multi-solute system, is adopted. The reasons of the choice of the Markham-Benton equation are as follows. 1. The number of solutes of the Markham-Benton equation can be increased easily to infinity. 2. The equation has no parameter which is due to the interaction among the solutes. 3. The consequent calculation is simple. The Markham-Benton equation is represented by Equation(3-2).

$$q_i' = Q_i x_i C_i' / (1+\sum_i x_i C_i') \qquad (3\text{-}2)$$

For the simplicity of the later calculations, it is postulated that the ultimate uptake capacity of adsorbent Q_i depends on the Langmuir coefficient x_i. Then x_i becomes to have a one-to-one correspondency to solute "i". Consequently we can draw up the solutes in order of the largeness of x_i, and regard the coordinate of x_i as a kind of "Component Coordinate". When there are numerous solutes, we can approximately assume the wastewater to be a distributed system on the component coordinate.

Equation(3-2) can be rewritten as the following, Equation(3-3).

$$q(x) = Q(x)xC(x)/\{1+\int_0^\infty xC(x)dx\} \qquad (3\text{-}3)$$

where q(x) and C(x) are the probability density of the adsorbed TOC amount and the TOC concentration of liquid-phase respectively, and the latter gives the distribution as mentioned in 3-2-1. We call this distribution Characteristic Distribution of Langmuir Coefficient for Liquid Concentration (C.D.C.). The TOC concentration of wastewater, C_T, is given by Equation(3-4).

$$C_T = \int_0^\infty C(x)dx \qquad (3\text{-}4)$$

If the correlation formula for multi-solute system is correct and C(x) can be identified, we can predict the equilibria at arbitrary conditions from C(x) and Equation(3-3). Therefore the problem becomes essentially how to identify C(x).

3-2-3 Differential Adsorption Equilibrium curve

To describe an adsorption equilibrium, we usually use the adsorption isotherm (Figure 3-2),

which can be obtained generally from the batch experiment of adsorption equilibrium. When the initial concentrations of solution are constant and the amounts of adsorbent are varied in this batch experiment (Figure 3-4(b)), the curve in Figure 3-3 can be obtained, and it can be easily transformed into the curve in Figure 3-2. We name the curve in Figure 3-3 "Integral Adsorption Equilibrium curve (I.A.E. curve)".

Now let us consider the following operation of adsorption as shown in Figure 3-4(a). A small amount of adsorbent "dy" is thrown into the wastewater. After the equilibrium is achieved, the wastewater is filtered off and then the TOC concentration of the solution-phase is measured. Further the repeat of this operation with this filtrate successively gives a curve as shown in Figure 3-5, where y is the accumulated amount of used adsorbent. We also name it "Differential Adsorption Equilibrium curve (D.A.E. curve)".

Although the measurement of D.A.E. curve requires a somewhat tedious experimental procedure, it gives us the multi-solute adsorption behavior of the wastewater more explicitly than I.A.E. curve, because the more adsorbable solutes in wastewater decrease

more rapidly by the differential adsorption operation than by the integral adsorption operation as the operation proceeds. We can confirm the advantage of

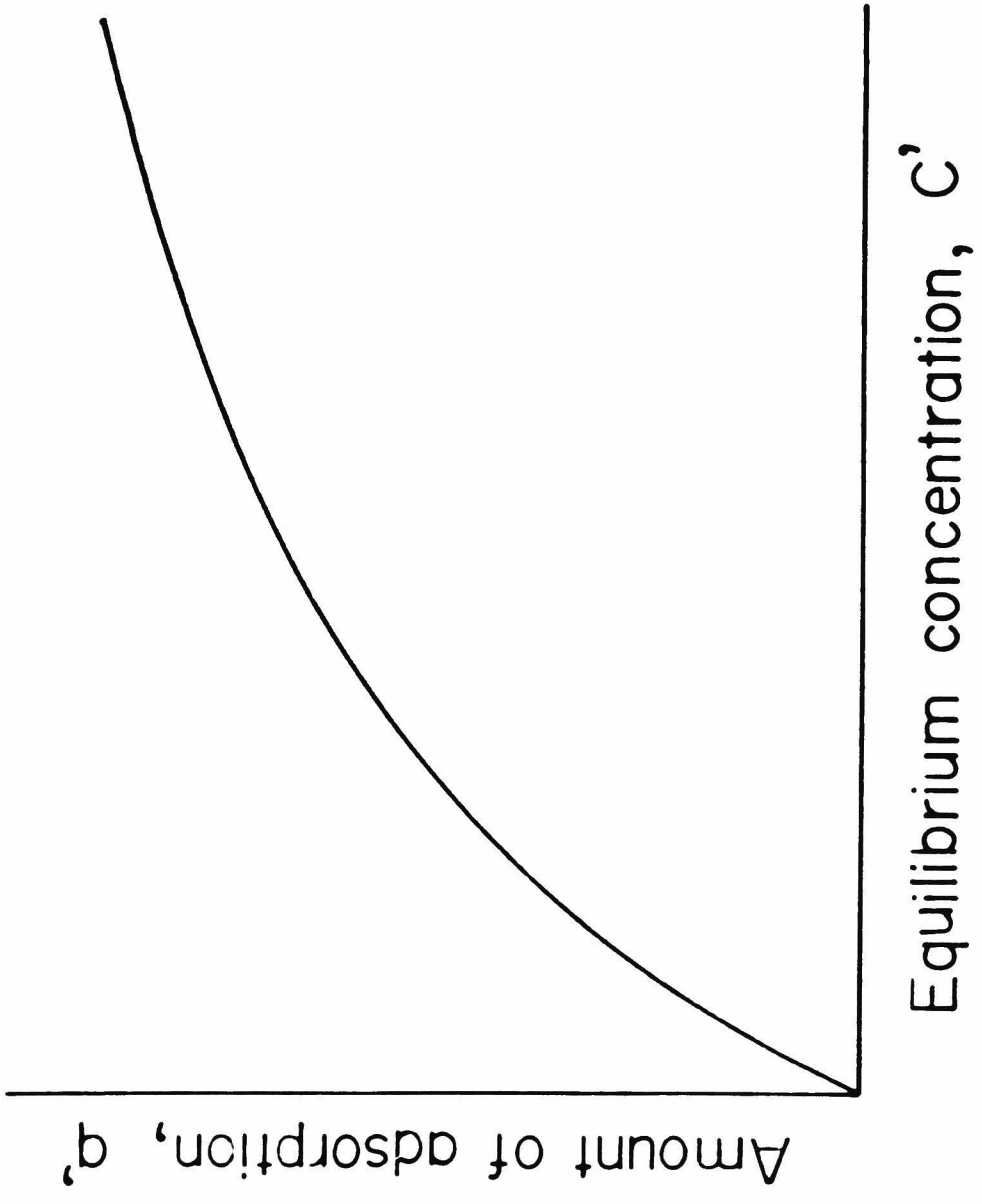

Fig.3-2 Adsorption isotherm

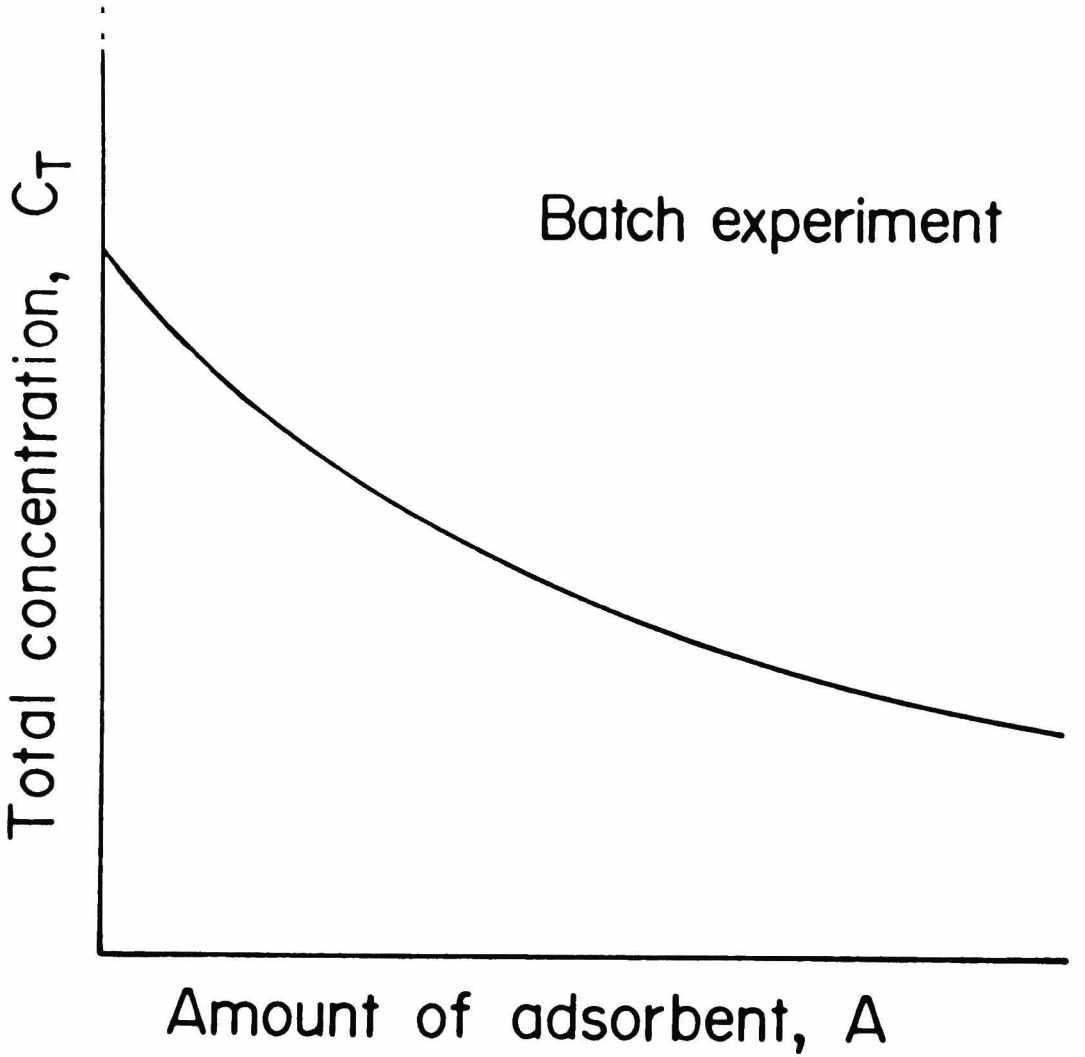

Fig.3-3 Integral adsorption equilibrium curve

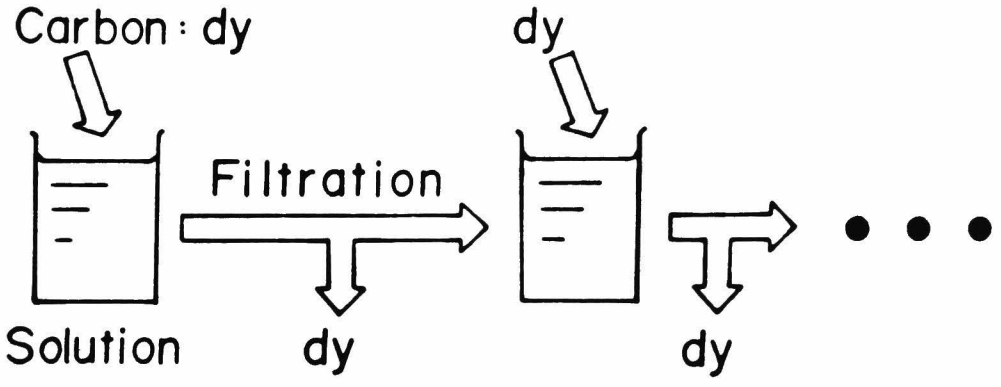

Fig.3-4(a) Differential operation of adsorption

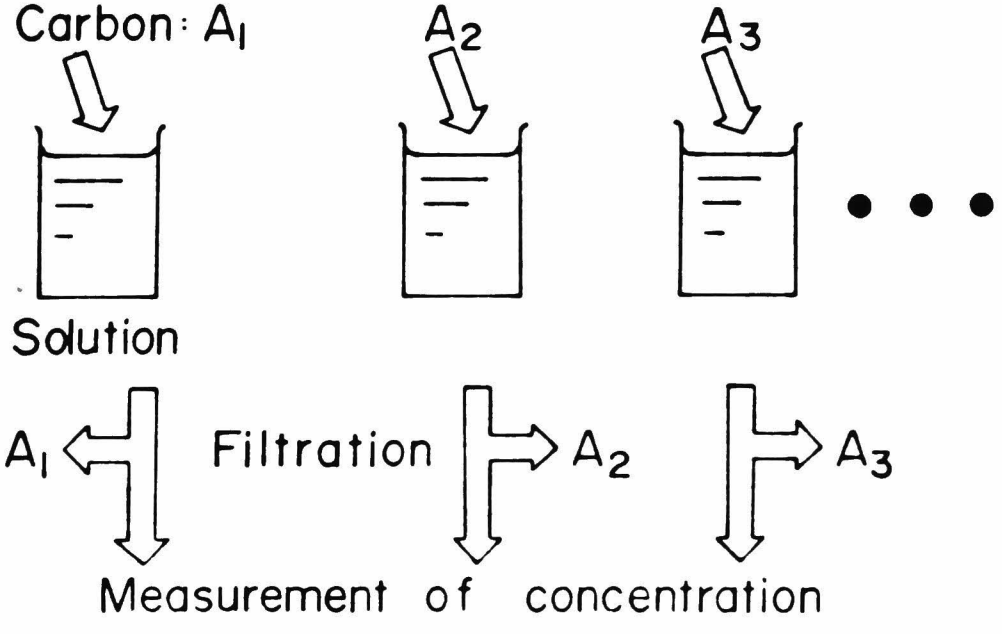

Fig.3-4(b) Integral operation of adsorption

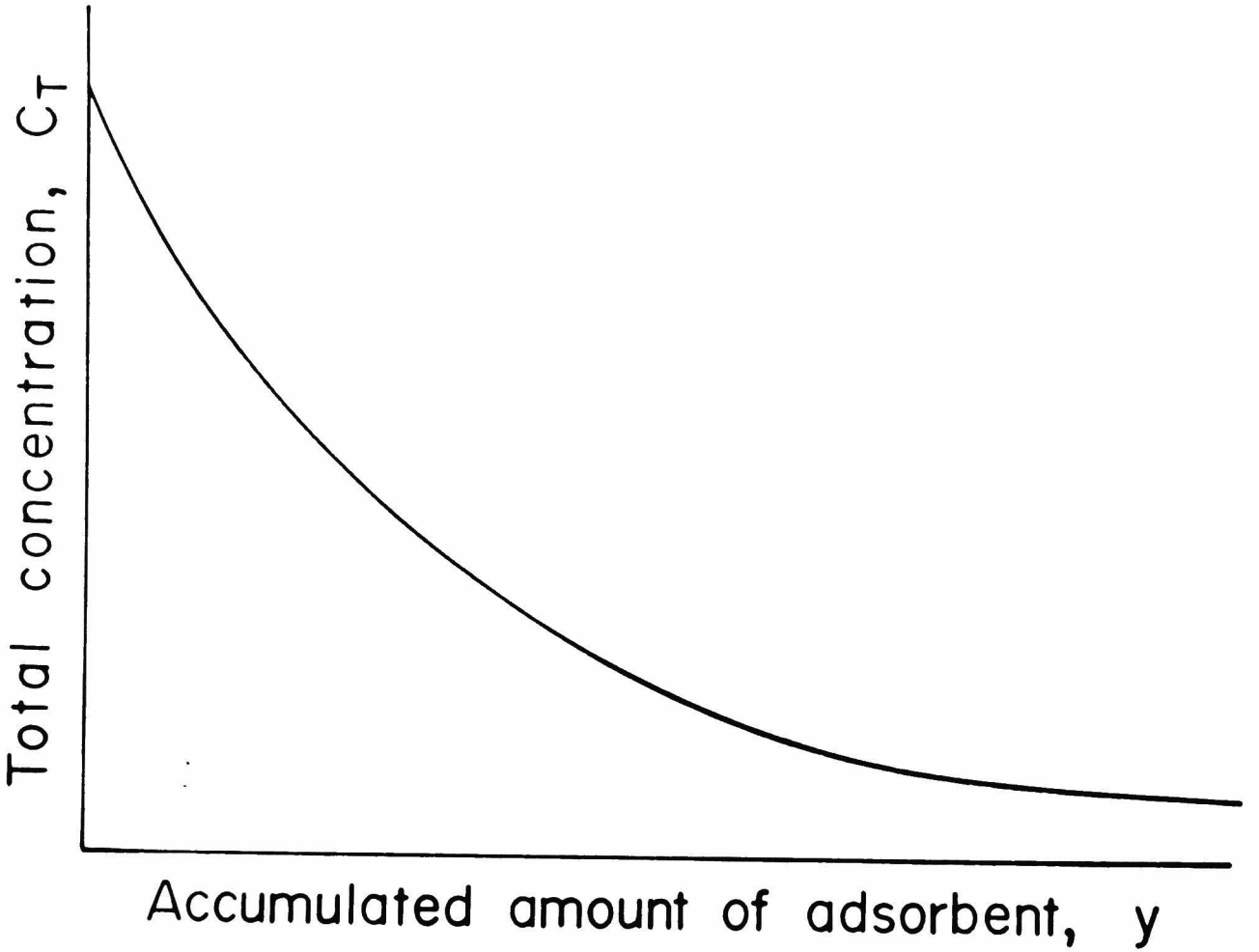

Fig.3-5 Differential adsorption equilibrium curve

the differential adsorption operation through the presentation of the difference of the changes of C.D.C. curves for each operations. The calculation results of the changes of C.D.C. curves of Wastewater II by the differential and integral adsorption operations are shown in Figure 3-6 as mentioned later. The C.D.C. curve of A = 0 or y = 0 in Figure 3-6 represents the initial C.D.C. of Wastewater II. Then as the differential adsorption operation proceeds and the accumulated amount of the used adsorbent, y, increases gradually from 0 to 2.8kg/m^3, the C.D.C. curve changes and becomes lower as shown by solid line. And the broken lines of A = 0.4 to 2.8kg/m^3 show the C.D.C. curves at the integral adsorption equilibria for the each amounts of adsorbent used, A. Further the area enclosed by each C.D.C. curve and the x axis equals the total concentration for the corresponding value of y or A, so the calculations of the total concentrations for various values of y or A give us the D.A.E. or I.A.E. curves, which are shown in Figures 3-3 and 3-5. Then from Figure 3-6 we can find that the peak of the C.D.C. more remarkably moves left by the differential adsorption operation than the integral operation, and that the

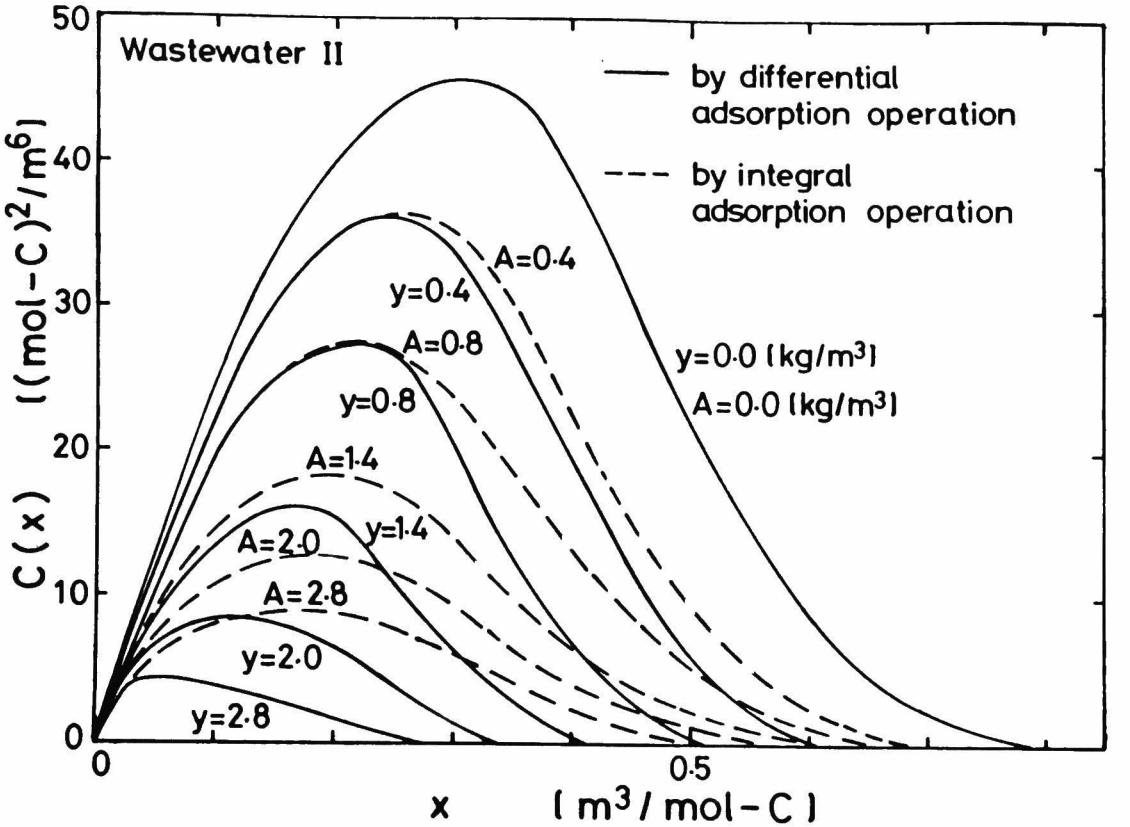

Fig.3-6 Change of C.D.C.

more adsorbable solutes in wastewater decrease more rapidly by the differential operation. Therefore the D.A.E. curve is thought to be more suitable to identify the C.D.C..

3-2-4 Identification of Characteristic Distribution of Langmuir Coefficient

Now we try to determine C.D.C. from D.A.E. curve. C.D.C. is a function of the Langmuir coefficient x and the accumulated amount of adsorbent y, and so it can be given by Equation(3-5).

$$C = C(x,y) \tag{3-5}$$

and the TOC concentration is given by Equation(3-6).

$$C_T(y) = \int_0^\infty C(x,y)dx \tag{3-6}$$

When the volume of solution is constant and it does not change throughout the differential adsorption operation, the material balance between before and after the differential adsorption gives Equation(3-7).

$$dC(x,y) = -q(x)dy \tag{3-7}$$

Substituting Equation(3-3) into Equation(3-7), we obtain Equation(3-8).

$$\frac{\partial C(x,y)}{\partial y} = - \frac{Q(x) x C(x,y)}{1+\int_0^\infty C(x,y) x dx} \qquad (3\text{-}8)$$

As we can regard C(x,y) as a exponential function from the form of the differential equation, Equation (3-8), here let us assume that the general solution of Equation(3-8) can be represented by Equation(3-9).

$$C(x,y) = C_T(0) G(x) \exp\{-f(y) x H(x)\} \qquad (3\text{-}9)$$

Then Equation(3-6) becomes Equation(3-10).

$$C_T(y) = C_T(0) \int_0^\infty G(x) \exp\{-f(y) x H(x)\} dx \qquad (3\text{-}10)$$

By substituting Equation(3-9) into Equation(3-8), we can obtain Equation(3-11).

$$\frac{H(x)}{Q(x)} \frac{\partial f(y)}{\partial y} = \frac{1}{1+C_T(0) \int_0^\infty G(x) \exp\{-f(y) x H(x)\} x dx} \qquad (3\text{-}11)$$

As the right-hand side of Equation(3-11) is independent of x, the relationship of Equation(3-12) must be held.

$$Q(x) = Q_0 H(x) \qquad (3\text{-}12)$$

Equation(3-13) is obtained from Equations(3-11) and (3-12).

$$\frac{\partial f(y)}{\partial y} = \frac{Q_0}{1+C_T(0) \int_0^\infty G(x) \exp\{-f(y) x H(x)\} x dx} \qquad (3\text{-}13)$$

Consequently, f(y) depends on G(x) and H(x) through Equation(3-13), and on the other hand, D.A.E. curve can be experimentally obtained. The problem reduces to how to solve the non-linear Fredholm integral equation of the first kind, Equation(3-10), using the observed D.A.E. curve.

Although there are various methods to solve Equation(3-13), the method of parameter fitting was used in the present study. Let us adopt Equation (3-14) as a simulating formula for G(x), because it is a series and is convenient for the consequent calculation. And H(x) is also assumed to be represented by Equation(3-15), because it is the best among some representation of H(x), which were tested actually.

$$G(x) = a_0 e^{b_0 x} + a_1 x e^{b_1 x} + \cdots + a_n x^n e^{b_n x} + \cdots \tag{3-14}$$

$$H(x) = 1 + \alpha_1 x + \alpha_2 x^2 + \cdots + \alpha_n x^n + \cdots \tag{3-15}$$

Giving the appropriate values for f(0), Q_0, a_n's, b_n's and α_n's, we can numerically solve the differential equation on f(y), Equation(3-13). By substitution of f(y) obtained here into Equation(3-10), $C_T(y)$ can be obtained. By searching optimal values of

these parameters so as to fit $C_T(y)$ to the observed D.A.E. curve, we can finally identify the initial C.D.C..

3-2-5 Prediction of adsorption equilibrium (I.A.E. curve) from Characteristic Distribution of Langmuir Coefficient

In the previous section, the determination method of the C.D.C. from D.A.E. curve was presented. However, to prove the reliability of the C.D.C., the relationship between C.D.C. and the integral adsorption operation, which has been used extensively up to now, must be considered. Further the integral adsorption equilibrium must be predicted using the C.D.C. determined from the D.A.E. curve, and the prediction results must be compared with the experimental data. The prediction method of the integral adsorption equilibrium from the C.D.C. is considered in this section.

When an amount of activated carbon, A, is thrown into a wastewater whose distribution of Langmuir coefficient is given as $C_1(x)$, the resulting distribution $C_2(x)$ after achieving the equilibrium is given

by Equation(3-16) from the mass balance.

$$C_1(x) = C_2(x) + Aq(x) \tag{3-16}$$

Substituting Equation(3-3) into Equation(3-16), we obtain the next equation.

$$\frac{AQ(x)C_2(x)x}{1+\int_0^\infty C_2(x)xdx} + C_2(x) = C_1(x) \tag{3-17}$$

or

$$C_2(x) = C_1(x)/\{1+KxQ(x)\} \tag{3-18}$$

where

$$K = A/\{1+\int_0^\infty C_2(x)xdx\} \tag{3-19}$$

Equation(3-20) is derived from Equation(3-19).

$$\int_0^\infty C_2(x)xdx = (A/K)-1 \tag{3-20}$$

Then next equation is obtained from Equations(3-18) and (3-20).

$$\int_0^\infty xC_1(x)/\{1+KxQ(x)\}dx = (A/K)-1 \tag{3-21}$$

On the other hand, the final TOC concentration, C_{T2}, can be given by Equation(3-22).

$$C_{T2} = \int_0^\infty C_2(x)dx$$

$$= \int_0^{\infty} C_1(x)/\{1+KxQ(x)\}dx \qquad (3\text{-}22)$$

By the determination of K by trial and error method so as to satisfy Equation(3-21), $C_2(x)$ and C_{T2} can be obtained from Equations(3-18) and (3-22). Therefore we can predict I.A.E. curve through the repeats of the above calculating procedure.

3-2-6 Constant Q method (Method II)

In the preceding section, we considered the case in which the ultimate uptake capacity Q is dependent on x (Method I). However, when we consider a simple case in which Q is independent of x, the calculation by computer is much easier than Method I (in which Q depends on x). For some kinds of wastewater, this method might be useful. Therefore let us consider a simple case, in which Q is independent of x, in this section. In the present case, the next equation holds.

$$Q(x) = Q_0 = \text{const} \qquad (3\text{-}23)$$

or, from Equations(3-12) and (3-23)

$$H(x) = 1 \qquad (3\text{-}24)$$

Therefore Equation(3-13) becomes Equation(3-25).

$$\frac{\partial f(y)}{\partial y} = \frac{Q_0}{1+C_T(0)\int_0^\infty G(x)x\cdot\exp\{-f(y)x\}dx} \qquad (3\text{-}25)$$

The integral term of Equation(3-25) can be expressed as follows.

$$\int_0^\infty G(x)x\cdot\exp\{-f(y)x\}dx$$

$$= \int_0^\infty a_0 x\cdot\exp[-\{f(y)-b_0\}x]dx$$

$$+ \int_0^\infty a_1 x^2\cdot\exp[-\{f(y)-b_1\}x]dx + \cdots$$

$$+ \int_0^\infty a_n x^{n+1}\cdot\exp[-\{f(y)-b_n\}x]dx + \cdots$$

$$= \frac{a_0}{\{f(y)-b_0\}^2} + \frac{2a_1}{\{f(y)-b_1\}^3} + \cdots + \frac{(n+1)!a_n}{\{f(y)-b_n\}^{n+2}} + \cdots \qquad (3\text{-}26)$$

Then the integration of Equation(3-25) gives Equation (3-27).

$$\int_0^Y Q_0 dy = C_T(0)\int_{f(0)}^{f(y)} [\frac{1}{C_T(0)} + \frac{a_0}{\{f(y)-b_0\}^2} + \frac{2a_1}{\{f(y)-b_1\}^3} + \cdots + \frac{(n+1)!a_n}{\{f(y)-b_n\}^{n+2}} + \cdots]df(y)$$

$$= C_T(0)\left[\frac{f(y)}{C_T(0)} - \frac{a_0}{f(y)-b_0} - \frac{a_1}{\{f(y)-b_1\}^2}\right.$$

$$- \frac{2a_2}{\{f(y)-b_2\}^3} - \cdots - \frac{n!a_n}{\{f(y)-b_n\}^{n+1}}$$

$$\left. - \cdots\right]_{f(0)}^{f(y)} \qquad (3\text{-}27)$$

On the other hand, we get Equation(3-28) from Equation(3-6).

$$C_T(y) = C_T(0)\int_0^\infty G(x)\exp\{-f(y)x\}dx$$

$$= C_T(0)\left[\frac{a_0}{f(y)-b_0} + \frac{a_1}{\{f(y)-b_1\}^2} + \frac{2a_2}{\{f(y)-b_2\}^3}\right.$$

$$\left. + \cdots + \frac{n!a_n}{\{f(y)-b_n\}^{n+1}} + \cdots\right] \qquad (3\text{-}28)$$

From Equations(3-27) and (3-28), we get Equation (3-29).

$$[f(y) - C_T(y)]_{f(0)}^{f(y)} = Q_0 y \qquad (3\text{-}29)$$

or

$$f(y) - f(0) = Q_0 y + C_T(y) - C_T(0) \qquad (3\text{-}30)$$

When $C_T(y)$, $C_T(0)$ are given, the fitting of parameters, Q_0, a_n's and $\{f(0)-b_n\}$'s can be performed

using Equations(3-28) and (3-30). So the calculation by computer is much easier than the case in which Q(x) is not constant (Method I).

The relationship between C.D.C. and I.A.E. curve is completely the same as in Method I. However, the integration of Equation(3-22) becomes much simpler, because it can be made analytically by a term-to-term integration.

3-2-7 Lumped parameter method (Method III)

To verify the availability of the proposed prediction methods (Method I and II), the lumped parameter method, Method III, in which the solutes in wastewaters are considered to consist of one unadsorbable and one adsorbable solute, which obeys the Langmuir equation, is adopted. The reason of adoption of Method III is as follows. If we try to represent the adsorption equilibrium of wastewater, which contains many unknown solutes, a method in which the solutes are regarded as single solute in terms of the total concentration may be adopted as the simplest one.

In Method III, the adsorbable solutes in waste-

water are regarded as one solute, and further one unadsorbable solute is added in order to extend the applicability of the simplest one.

In this method, Equations(3-31) and (3-32) are corresponding to Equations(3-6) and (3-8), respectively.

$$C_T(y) = C'_{ad}(y) + C'_{unad}(0) \tag{3-31}$$

$$\frac{dC'_{ad}(y)}{dy} = - \frac{Q_{ad}x_{ad}C'_{ad}(y)}{1+C'_{ad}(y)x_{ad}} \tag{3-32}$$

Then the parameters to be fitted to D.A.E. curve are the ratio of initial concentrations of the adsorbate and the other solute, $K_{0c} = C'_{ad}(0)/C'_{unad}(0)$, the Langmuir coefficient, x_{ad}, and the ultimate uptake capacity, Q_{ad}, because $C_T(0)$ $(= C'_{ad}(0) + C'_{unad}(0))$ is known.

On the other hand, the prediction of I.A.E. curve can be performed by Equations(3-33) and (3-34).

$$C'_{1ad} = C'_{2ad} + AQ_{ad}x_{ad}C'_{2ad}/(1 + x_{ad}C'_{2ad}) \tag{3-33}$$

$$C_{T2} = C'_{2ad} + C'_{1unad} \tag{3-34}$$

That is, C_{T2} can be obtained from Equation(3-34) by searching C'_{2ad} so as to satisfy Equation(3-33).

3-3 Experiments

To verify the availability of the proposed description method, adsorption experiments were performed using four kinds of synthetic and one kind of industrial wastewater. The synthetic wastewaters were the aqueous solutions which involved 5 ∿ 11 solutes chosen among aniline, cyclohexanol, p-chlorophenol, p-cresol, β-dinitrophenol, polyethylene glycol ($M \fallingdotseq 400$), phenol, n-hexyl alcohol, hydroquinone, nitrobenzene, p-nitrophenol and m-nitrophenol, and the industrial wastewater mainly contained molasses. The compositions of wastewaters are summarized in Table 3-1. As shown in Table 3-1, the adsorbabilities of the synthetic wastewaters were thought to be practically changed by the addition of the solute which had large molecular weight and by the change of the ratio of the concentrations of solutes, which had various adsorption characteristics. The verification was also performed using the industrial wastewater whose solutes were unknown.

Two D.A.E. curves and one I.A.E. curve were measured for each wastewater. All experiments were performed at 35°C. A commercial activated carbon CAL

Table 3-1 Component of Wastewater

Wastewater I Synthetic		Wastewater II Synthetic	
nitrobenzene	0.315*	nitrobenzene	0.044
cyclohexanol	0.052	cyclohexanol	0.349
p-cresol	0.183	p-cresol	0.343
phenol	0.368	phenol	0.088
p-nitrophenol	0.082	p-nitrophenol	0.176

Wastewater III Synthetic		Wastewater IV Synthetic	
m-nitrophenol	0.091	nitrobenzene	0.092
p-nitrophenol	0.091	phenol	0.093
p-cresol	0.089	polyethylene glycol (M ≒ 400)	0.627
β-dinitrophenol	0.091	p-nitrophenol	0.093
n-hexyl alcohol	0.092	p-cresol	0.095
p-chlorophenol	0.092		
aniline	0.092	Wastewater V Industrial Molasses is mainly contained.	
hydroquinone	0.090		
nitrobenzene	0.090		
cyclohexanol	0.090		
phenol	0.092		

* mole fraction based on mol-Carbon(mol-C) [-]

(14 ∿ 16 mesh) from Calgon Corp. was used as adsorbent. Before use, the carbon was pulverized in ball mill and the powdered carbon under 200 mesh was used. The powdered carbon was further washed and dried at 110°C for a day. Further it was kept in a desiccator containing silicagel. Adsorption equilibria were obtained by contacting known weights of carbon with a given wastewater. The carbon was degassed for 30 minutes by aspirator as soon as it contacted with the wastewater. After the equilibrium was attained, a sample was filtered through a 0.5μ-glass filter to be free of any trace of suspended carbon. The total concentration of each sample was measured by TOC analyzer. In the experiment of differential adsorption equilibrium, the above processes were repeated.

It was confirmed by preliminary experiment that when a small amount of adsorbent "dy" which was thrown into the wastewater at the each stage of differential adsorption operation was 0.2g/1000cm^3 for all synthetic wastewater, and 2.0g/1000cm^3 for the industrial wastewater, the adsorption was regarded as sufficiently "differential". That is, for example, the results (D.A.E. curves) of the experiments, in

which dy = 2.0g/1000cm^3,and dy = 1.0g/1000cm^3 (< 2.0g/1000cm^3), were quite agreed for the industrial wastewater, so the differential adsorption operation in which dy = 2.0g/1000cm^3 was regarded as sufficiently "differential".

The samples for the differential adsorption operation were continuously shaken for more than 2 hours for the synthetic wastewaters and 1 day for the industrial wastewater. For the integral adsorption operation, the samples were shaken for more than 2 days.

3-4 Results and Calculation Procedures

The D.A.E. and I.A.E. curves for Wastewater I to V, which were obtained from experiments, are shown in Figures 3-7 to 3-11 and Figures 3-12 to 3-16, respectively.

As we obtain more experimental curves of D.A.E., whose initial concentrations cover wide range of concentration, to determine the C.D.C., we can more intensively identify it, because the quality of information obtained from D.A.E. curves becomes

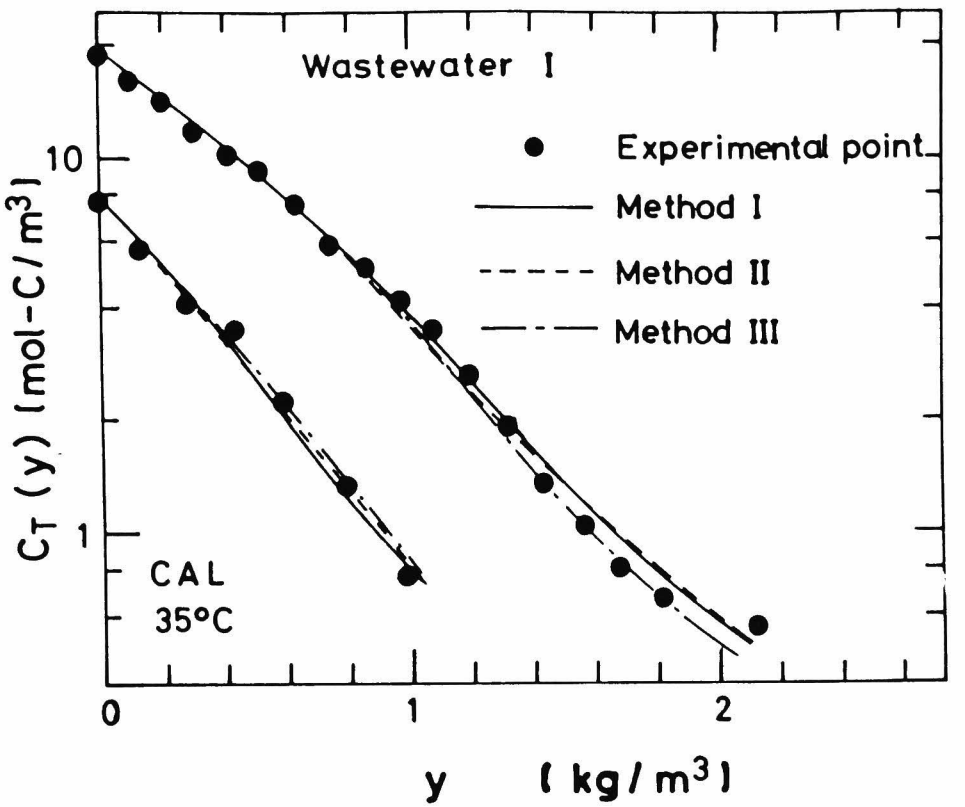

Fig.3-7 Differential adsorption equilibrium curves

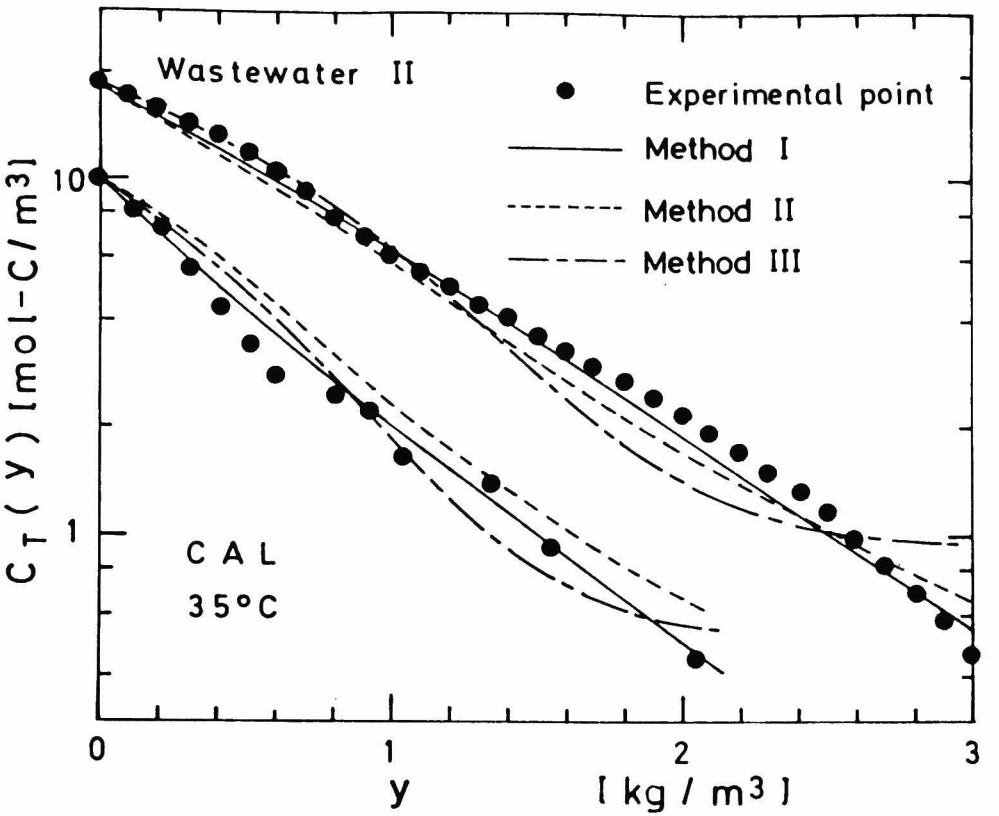

Fig.3-8 Differential adsorption equilibrium curves

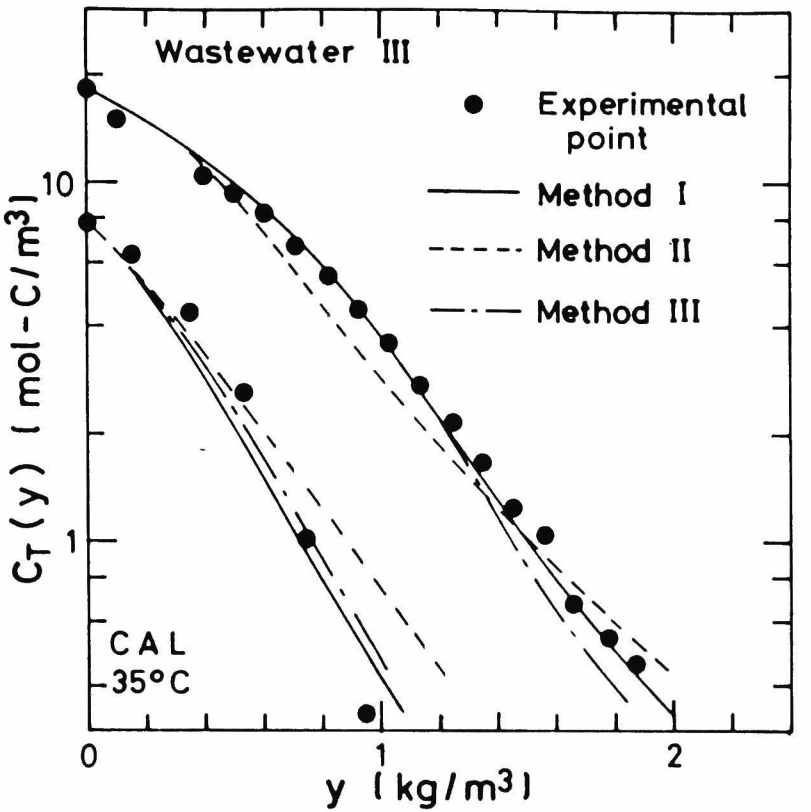

Fig.3-9 Differential adsorption equilibrium curves

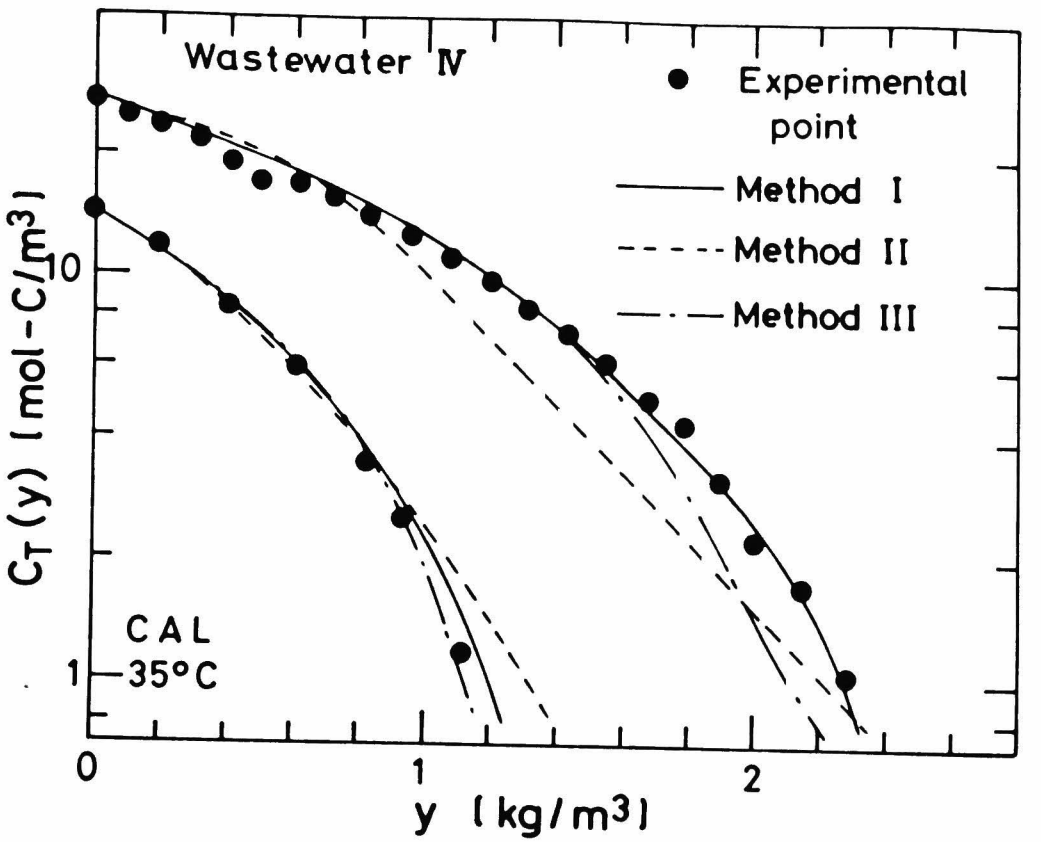

Fig.3-10 Differential adsorption equilibrium curves

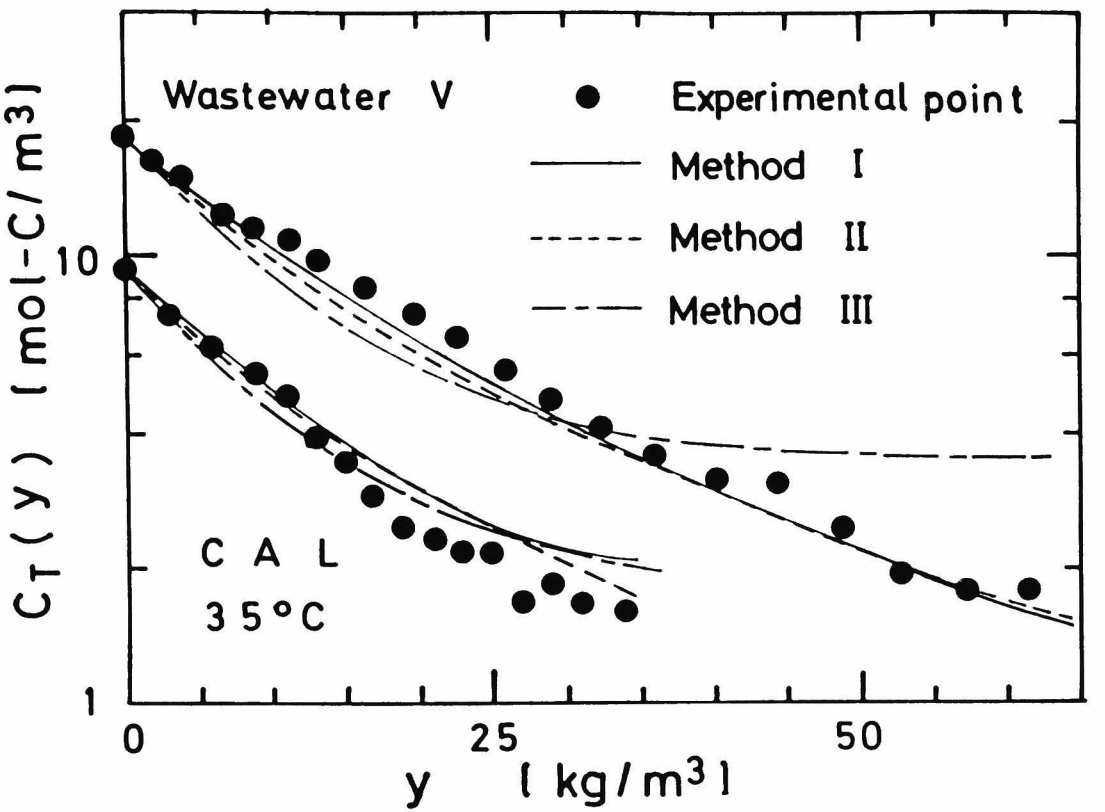

Fig.3-11 Differential adsorption equilibrium curves

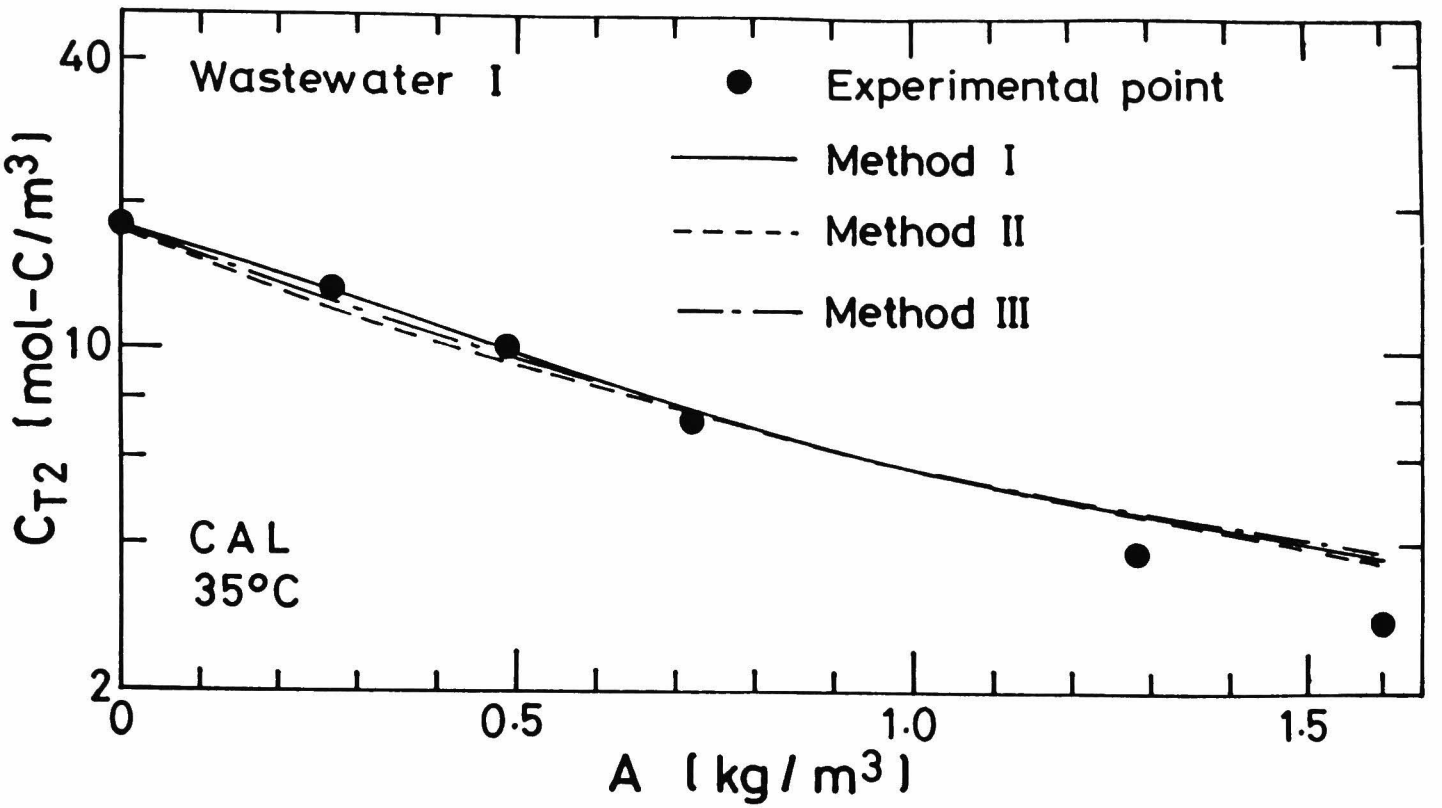

Fig.3-12 Integral adsorption equilibrium curves

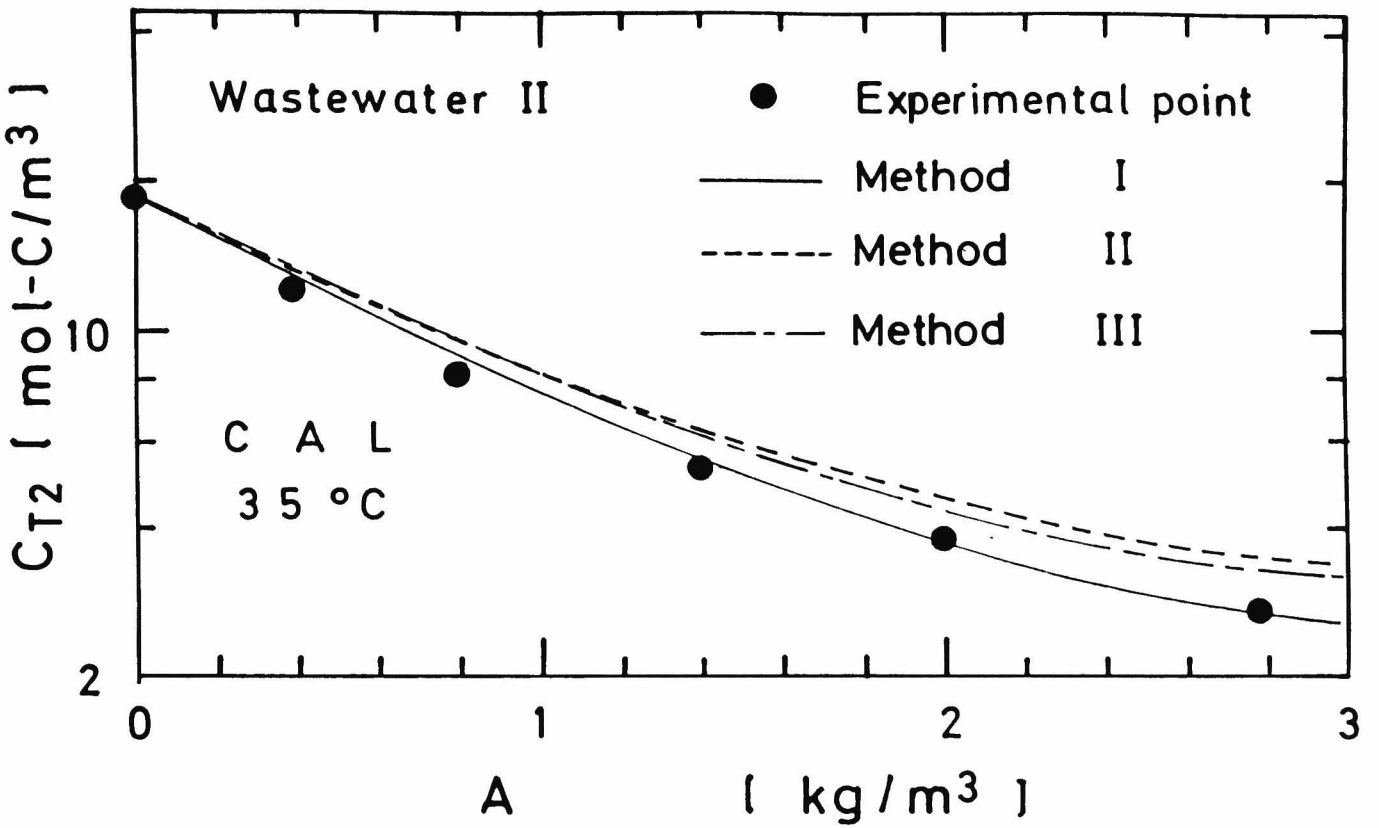

Fig.3-13 Integral adsorption equilibrium curves

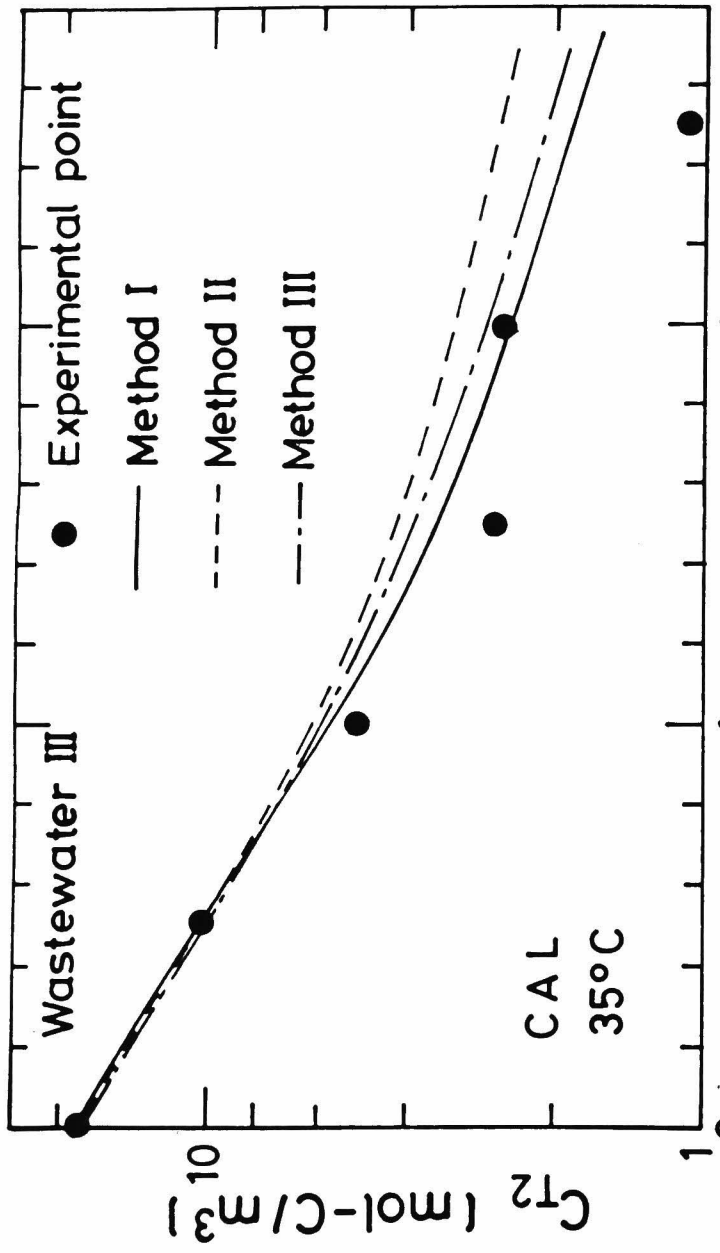

Fig.3-14 Integral adsorption equilibrium curves

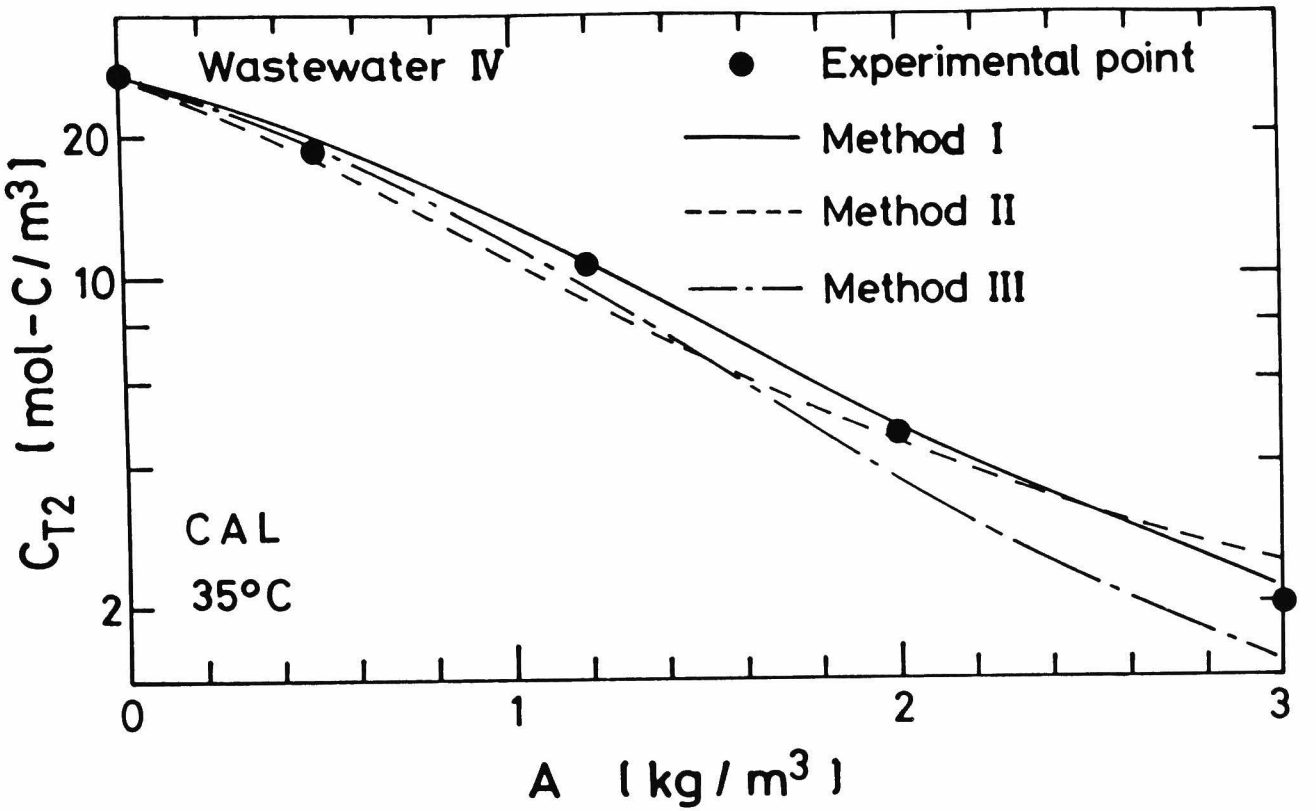

Fig.3-15 Integral adsorption equilibrium curves

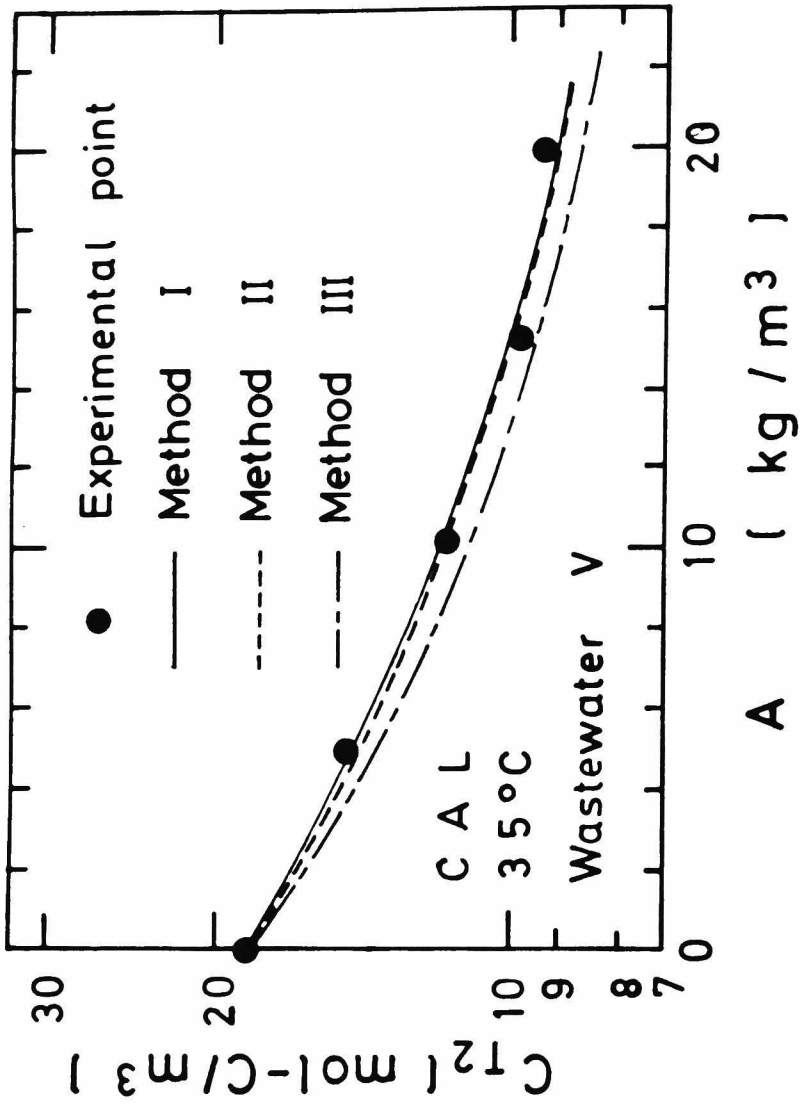

Fig.3-16 Integral adsorption equilibrium curves

better. To obtain the correct information as easily, two D.A.E. curves with different initial concentrations were measured as shown in Figures 3-7 to 3-11.

Next, the parameters of the three methods (Method I to III) were determined by the uses of the two D.A.E. curves in Figures 3-7 to 3-11, and the values of the parameters are shown in Table 3-2. In this calculation, for Method I the second term (n = 1) of Equation(3-14) and the three terms (n = 0 ∿ 2) of Equation(3-15) were adopted to save the computational load of parameter fitting. That is, Equations(3-35) and (3-36) were used as G(x) and H(x).

$$G(x) = a_1 x \cdot \exp(b_1 x) \tag{3-35}$$

$$H(x) = 1 + \alpha_1 x + \alpha_2 x^2 \tag{3-36}$$

The six parameters of Method I, a_1, b_1, α_1, α_2, f(0) and Q_0, were determined by the uses of Equations (3-10) and (3-13) and the observed $C_T(0)$ and $C_T(y)$. In this case, Runge-Kutta-Gill method was used to solve the differential equation (Equation(3-13)) and SIMPLEX method to search the parameters. Equation (3-37) was used as the performance index of SIMPLEX method.

Table 3-2 Parameters and Accuracies of Each Method

Wastewater	I	II	III	IV	V
Method I					
a_1	178.3	16.48	24.65	12.27	14210.
b_1	-2.816	-1.447	-1.669	-1.116	0.3942
α_1	-5.878	-4.995	-2.245	-1.952	-0.9220
α_2	16.38	13.11	2.812	1.278	-0.3759
f(0)	18.08	1.308	4.713	6.495	122.4
Q_0	54.95	18.94	33.51	46.10	4.742
Fitting accuracy* of D.A.E. curve	0.0714	0.0796	0.0997	0.0971	0.0936
Prediction accuracy* of I.A.E. curve	0.1519	0.0492	0.2988	0.0595	0.0252
Method II					
a_1	1.004	2.041	0.8195	0.4159	0.1916
a_2	4.173×10^{3}	1.257×10^{4}	4.772×10^{3}	1.535×10^{2}	9.595×10^{8}
a_3	-3.122×10^{4}	0.0	-3.343×10^{4}	0.0	-5.173×10^{11}
$f(0)-b_1$	3.418	58.74	2.788	7.920	1025.
$f(0)-b_2$	8.020	29.30	6.853	6.950	769.1
$f(0)-b_3$	10.53	0.0	9.137	0.0	991.0
Q_0	33.53	26.21	39.57	17.70	23.91

Table 3-2 (continued)

Wastewater	I	II	III	IV	V
Method II					
Fitting accuracy* of D.A.E. curve	0.0740	0.2221	0.1298	0.1735	0.1240
Prediction accuracy* of I.A.E. curve	0.1435	0.1903	0.5570	0.1242	0.0245
Method III					
K_{0c}	60.74	20.03	103.7	22.52	5.211
x_{ad}	0.07862	0.1807	0.1749	0.7992	0.005007
Q_{ad}	37.79	18.79	24.40	15.16	20.28
Fitting accuracy* of D.A.E. curve	0.0551	0.2183	0.1901	0.1148	0.2232
Prediction accuracy* of I.A.E. curve	0.1805	0.1658	0.4231	0.1555	0.0464

* $F = (1/N) \sum_{i=1}^{N} (|C_{Ti,calc} - C_{Ti,exp}|/C_{Ti,exp})$, N : No. of experimental points

$$F = -\sqrt{\left[\sum_{i=n+1}^{N}\{(1-C_{Ti,calc}(y)/C_{Ti,exp}(y))^2 C_{Ti,exp}(y)\}\right.}$$

$$\left.+\ 50\sum_{i=1}^{n}\{(1-C_{Ti,calc}(0)/C_{Ti,exp}(0))^2 C_{Ti,exp}(0)\}\right]/N \qquad (3\text{-}37)$$

On the other hand, for Method II the following equation was used as G(x), because of the same reason as Method I.

$$G(x) = a_1 x e^{b_1 x} + a_2 x^2 e^{b_2 x} + a_3 x^3 e^{b_3 x} \qquad (3\text{-}38)$$

Therefore the parameters of Method II were searched using Equations(3-28) and (3-30) and the observed $C_T(0)$ and $C_T(y)$. In this case, the unknown parameters were a_1, a_2, a_3, $f(0)-b_1$, $f(0)-b_2$, $f(0)-b_3$ and Q_0. However the two parameters, a_2 and a_3, could be eliminated by Equations(3-39) and (3-40), which were derived from Equation(3-28), when the initial concentrations and first derivatives of the D.A.E. curves were given by the experiments.

$$\left.\frac{dC_T(y)}{dy}\right|_{y=0} = -C_T(0)\left[\frac{a_0}{\{f(0)-b_0\}^2} + \frac{2a_1}{\{f(0)-b_1\}^3}\right.$$

$$\left. + \frac{6a_2}{\{f(0)-b_2\}^4} + \cdots + \frac{(n+1)!\,a_n}{\{f(0)-b_n\}^{n+2}} + \cdots\right] \qquad (3\text{-}39)$$

$$C_T(0) = C_T(0)\left[\frac{a_0}{f(0)-b_0} + \frac{a_1}{\{f(0)-b_1\}^2} + \frac{2a_2}{\{f(0)-b_2\}^3}\right.$$

$$\left. + \cdots + \frac{n!a_n}{\{f(0)-b_n\}^{n+1}} + \cdots\right] \qquad (3\text{-}40)$$

So finally the five parameters, a_1, $f(0)-b_1$, $f(0)-b_2$, $f(0)-b_3$ and Q_0, were searched by SIMPLEX method using Equation(3-41) as the performance index.

$$F = -\sqrt{\sum_{i=n+1}^{N}[\{1-C_{Ti,calc}(y)/C_{Ti,exp}(y)\}^2 C_{Ti,exp}(y)]}\Big/(N-n) \qquad (3\text{-}41)$$

Therefore the calculation of the parameter determination is much simpler than Method I, because Method II does not need Runge-Kutta-Gill method to solve differential equation.

For Method III the three parameters, x_{ad}, Q_{ad} and K_{0c} (= $C'_{ad}(0)/C'_{unad}(0)$), were determined using Equations(3-31) and (3-32) and the observed $C_T(0)$ and $C_T(y)$. In this calculation, Runge-Kutta-Gill method was used to solve the differential equation (Equation (3-32)) and the three parameters were also determined by SIMPLEX method using Equation(3-41) as the performance index.

The parameters determined as mentioned above

for each method, are shown in Table 3-2. Further the D.A.E. curves, which were calculated by Equations (3-10), (3-13), (3-35) and (3-36) for Method I, Equations(3-28) (n = 1 ∿ 3) and (3-30) for Method II, and Equations(3-31) and (3-32) for Method III, using the parameters in Table 3-2, are shown in Figures 3-7 to 3-11. The fitting accuracies of the calculated D.A.E. curves to the experimental curves were calculated by Equation(3-42) and also shown in Table 3-2.

$$F_a = (1/N) \sum_{i=1}^{N} (|C_{Ti,calc} - C_{Ti,exp}| / C_{Ti,exp}) \qquad (3\text{-}42)$$

On the other hand, the change of the form of C.D.C. curve of Wastewater II by the differential adsorption operation was calculated for Method I and the result is represented in Figure 3-17. The change shown in Figure 3-17 is corresponding to the D.A.E. curve which has the higher initial concentration in Figure 3-8. The C.D.C. curves have a peak as shown in Figure 3-17, because a term (n = 1) was adopted in Equation(3-14) to represent the C.D.C. (that is, Equation(3-35)) for Method I.

Next by the use of the parameters of Method I to

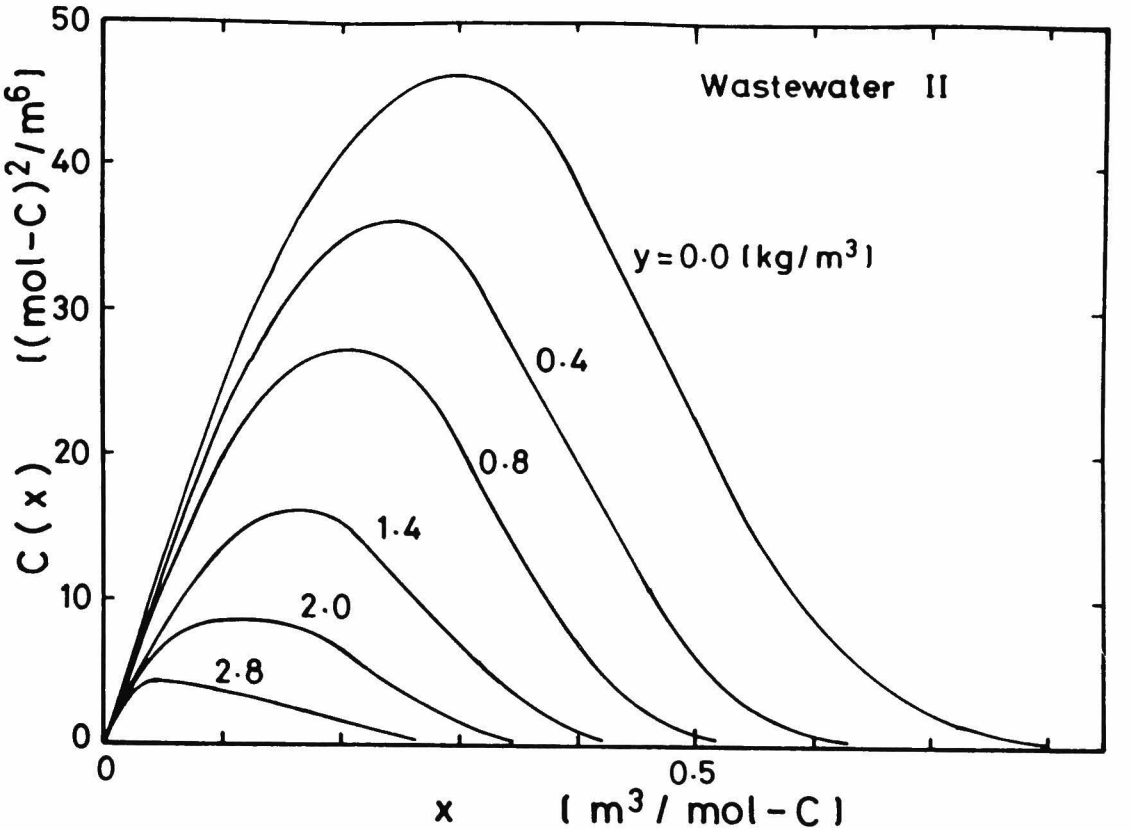

Fig.3-17 Change of C.D.C. by differential adsorption operation

III in Table 3-2, the integral adsorption equilibria are predicted and the I.A.E. curves are obtained.

For Method I, C(x,0) can be obtained from the determined parameters by Equations(3-9), (3-35) and (3-36) and the initial total concentration of integral adsorption, $C_T(0)$. And $C_1(x)$ in Equations (3-21) and (3-22) is the obtained C(x,0). Q(x) can be obtained by Equations(3-12) and (3-36). Therefore we can determine the value of K for a given A so as to satisfy Equation(3-21). Substituting the determined K into Equation(3-22), C_{T2} can be predicted for the given A. The repeat of the above calculation for various values of A gives us a I.A.E. curve.

For Method II, C(x,0) can be also obtained by the uses of the determined parameters and initial concentration, $C_T(0)$, through Equations(3-9), (3-24) and (3-38), and equals $C_1(x)$. Q(x) is constant independently of x, that is, Q_0 (Equation(3-23)). Therefore C_{T2} can be obtained for a given A by Equations(3-21) and (3-22). In this calculation, Method II is much easier than Method I, because the integration can be made analytically by a term-to-term integration.

For Method III, as C'_{1ad} and C'_{1unad} can be obtained by the uses of the initial total concentration of the integral adsorption and the parameter, K_{0c}, we can calculate C'_{2ad} for a given A using the parameters, x_{ad} and Q_{ad}, and Equation(3-33). Then C_{T2} is obtained by Equation(3-34).

The I.A.E. curves, which were predicted by the procedures mentioned above, are shown in Figures 3-12 to 3-16. Further the prediction accuracies of these I.A.E. curves were calculated by Equation(3-42) and represented in Table 3-2.

On the other hand, the change of C.D.C. curve of Wastewater II by the integral adsorption was calculated for Method I and the result is shown in Figure 3-18.

3-5 Discussions

The purpose of Chapter 3 is to propose an approximate description based on a concept, Characteristic Distribution of Langmuir Coefficient, which describes the characteristics of adsorption equilibrium of wastewater, and to confirm its

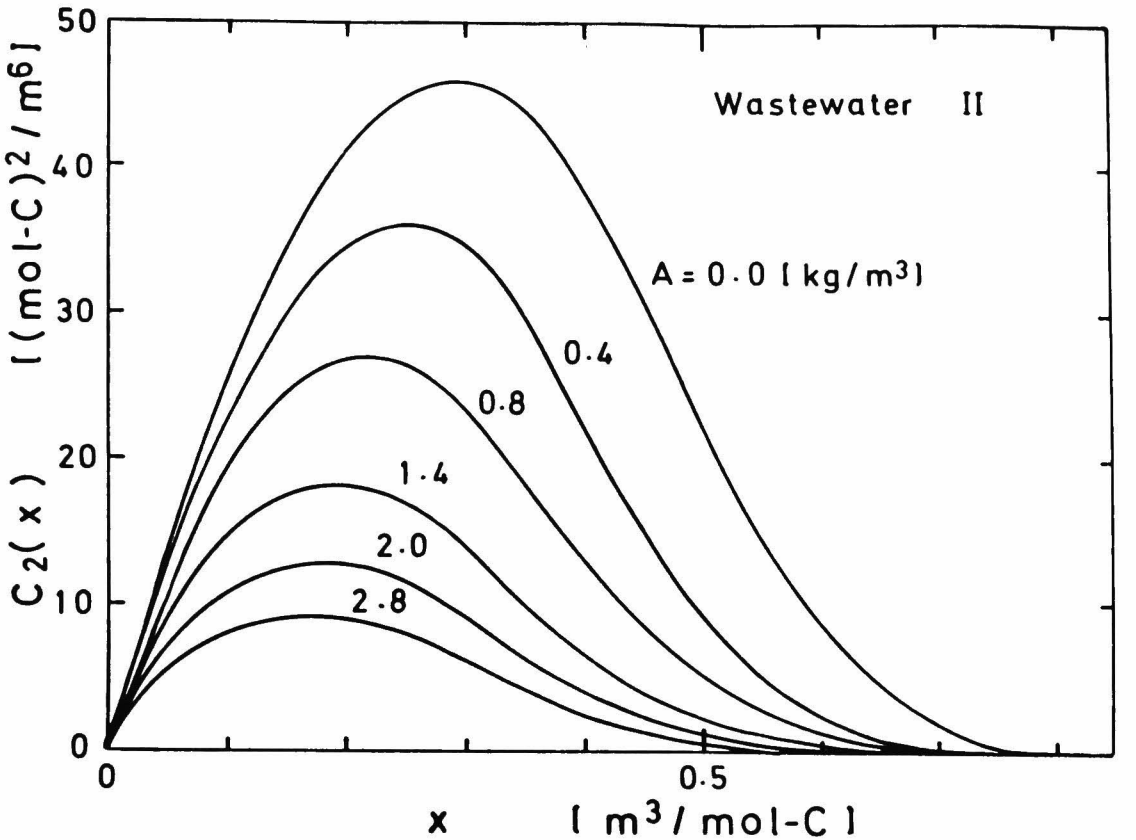

Fig.3-18 Change of C.D.C. by integral adsorption operation

reliability. Therefore accurate C.D.C. must be identified from experimental D.A.E. curve, and I.A.E. curve must be predicted exactly from the identified C.D.C..

It is also possible to identify C.D.C. from I.A.E. curve, but D.A.E. curve was used in spite of somewhat tedious experimental procedure in this chapter. The reason can be understood by the comparison between Figures 3-17 and 3-18. Figure 3-17 indicates an example of the change of C.D.C. curve by the differential adsorption operation, and is the calculation result of Wastewater II by Method I. The peak of the C.D.C. becomes lower and moves left as the differential adsorption operation proceeds. On the other hand, Figure 3-18 shows the calculation result of the change of C.D.C. curve by the integral adsorption operation for the same wastewater and method. The peak of the C.D.C. does not so remarkably move left as in Figure 3-17. Then it can be thought that the more adsorbable solutes in wastewater decrease more rapidly by differential adsorption operation than by integral adsorption operation as the operation proceeds, and so the feature of concentration distribution of wastewater is reflected

more remarkably on the obtained D.A.E. curve than I.A.E. curve. Therefore the D.A.E. curve is more suitable to identify the C.D.C..

Next let us examine the fitting accuracies of the D.A.E. curves to compare the accuracies of the C.D.C.'s obtained by the three methods. The following table is part of Table 3-2.

Table 3-3 Fitting Accuracies of Each Method

		Method I	Method II	Method III
Wastewater	I	0.0714	0.0740	0.0551
	II	0.0796	0.2221	0.2183
	III	0.0997	0.1298	0.1901
	IV	0.0971	0.1735	0.1148
	V	0.0936	0.1240	0.2232

We can find that the fitting accuracy by Method I is much better than the others in Table 3-3, and the difference between the accuracies by Method II and Method III is not remarkable. The reason for the excellence of Method I may be considered that two kinds of distributions, that is, $Q(x)$ and $C(x,0)$, are taken into consideration in Method I, while in Method II, only the distribution of C against x,

C(x,0), is permitted.

Next let us examine the prediction results of the I.A.E. curves. Table 3-4 is also part of Table 3-2 where the prediction accuracies by the three methods are presented.

Table 3-4 Prediction Accuracies of Each Method

		Method I	Method II	Method III
Wastewater	I	0.1519	0.1435	0.1805
	II	0.0492	0.1903	0.1658
	III	0.2988	0.5570	0.4231
	IV	0.0595	0.1242	0.1555
	V	0.0252	0.0245	0.0464

Method I always gives us the best prediction result among the three methods except that Method II is somewhat better than Method I for Wastewater I and V. Therefore we can find that the prediction method of I.A.E. curve by Method I is much better than the others similarly to the fitting of D.A.E. curve. The reason may be thought that the fitting of D.A.E. curve by Method I was good, so that the obtained C.D.C. of Method I was the most accurate among the three. Therefore it is very important to make the

fitting accuracy of D.A.E. curve better and to obtain more accurate C.D.C. in order to improve the prediction accuracy in future. Actually in Figures 3-7 to 3-11, even Method I, which gave us the best fitting in the three methods, did not fit quite satisfactorily to two D.A.E. curves. The following reasons may be considered. 1. the inaccuracy which is owing to the adoption of the Markham-Benton equation as an adsorption isotherm. 2. the insufficient approximation of C.D.C. (that is, Equations(3-35) and (3-36)). In these two, 2. may be more important.

As mentioned above, we could analyze the adsorption equilibrium data using the new proposed concept, C.D.C., and obtained a fair success. On the other hand, the difference of C.D.C. between before and after the adsorption operation can be one of the most useful index which describes the adsorption capacity of the used adsorbent, and so we can investigate quantitively about the adsorption capacity of the adsorbent in terms of the C.D.C.. Further the concept of C.D.C. can be applied not only to the adsorption equilibrium but also to the kinetics of adsorption for multi-solute system. That is, the distribution of Langmuir coefficient for

volumetric coefficient of mass transfer can be determined by a measurement of the adsorption rate which is performed in the apparatus of batch type. This will be discussed in Chapter 4. Then it will be possible, in principle, to predict the break-through curve of adsorption column, using the determined distribution for volumetric coefficient of mass transfer and the C.D.C..

Further it can be supposed that this concept could serve to the analysis or design of separation or reaction processes which are concerned with unknown multi-component systems.

3-6 Conclusions

1. An approximate description of the adsorption equilibrium of wastewater was developed in terms of such a comprehensive index of concentration as TOC, BOD or COD.

2. The constitutional steps of the description method are as follows: (1) Markham-Benton equation (multi-component Langmuir equation) is applied to describe the adsorption equilibrium of multi-component

system. (2) "One-to-one" correspondency between the Langmuir coefficient in Markham-Benton equation and the component in the wastewater is postulated, because the Langmuir coefficient can be considered to be a quantitative index representing the adsorption characteristics of component. (3) A new concept, "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration", defined on a plane which is composed of the axes of the Langmuir coefficient and the probability density of the concentration, is introduced. (4) Using a set of equilibrium data, Characteristic Distribution of Langmuir Coefficient can be identified through some procedures of calculation. (5) The equilibrium at an arbitrary condition can be predicted on the basis of the above distribution.

3. The prediction accuracy by this approximate description has been demonstrated by some adsorption experiments conducted on synthetic and industrial wastewaters using activated carbon.

4. The conception, "Characteristic Distribution of Langmuir Coefficient", can be used for correlation of kinetic data of adsorption and also can be thought to be useful for the theoretical prediction of break-

through curve in fixed bed adsorber. Further it can be supposed that this concept can serve to the analysis or design of separation or reaction processes which are concerned with unknown multi-component systems.

5. In spite of the troublesome calculation of Method II, the difference between the prediction results of integral adsorption equilibrium by Method II and III was not remarkable. So Method II is not so practical to describe the adsorption characteristic of the systems examined in this chapter at least.

Nomenclature

A = amount of adsorbent used [kg/m^3]

a_F = coefficient of Equation(3-1) [$(mol\text{-}C)^{1-b_F} m^{3b_F}/kg$]

a_n = parameter in Equation(3-14) [$(mol\text{-}C/m^3)^{n+1}$]

b_F = coefficient of Equation(3-1) [-]

b_n = parameter in Equation(3-14) [$mol\text{-}C/m^3$]

C = probability density of liquid-phase TOC concentration [$(mol\text{-}C)^2/m^6$]

C_i' = liquid-phase TOC concentration of i-component [$mol\text{-}C/m^3$]

C_T = liquid-phase total TOC concentration [$mol\text{-}C/m^3$]

C_{T2} = liquid-phase TOC concentration at integral adsorption equilibrium [$mol\text{-}C/m^3$]

$C_1(x)$ = initial probability density of liquid-phase TOC concentration [$(mol\text{-}C)^2/m^6$]

$C_2(x)$ = probability density of liquid-phase TOC concentration at integral adsorption equilibrium [$(mol\text{-}C)^2/m^6$]

C_1' = initial liquid-phase TOC concentration [$mol\text{-}C/m^3$]

C_2' = liquid-phase TOC concentration at integral adsorption equilibrium [mol-C/m^3]

F = performance index [$(mol\text{-}C/m^3)^{1/2}$]

F_a = fitting and prediction accuracy [-]

f(y) = function of y defined by Equation(3-9) [mol-C/m^3]

G(x) = function of x defined by Equation(3-9) [mol-C/m^3]

H(x) = dimensionless function of x defined by Equation(3-9) [-]

K = variable defined by Equation(3-19) [kg/m^3]

K_{0c} = parameter of Method III, $=C'_{ad}(0)/C'_{unad}(0)$ [-]

N = number of experimental points [-]

n = number of experimental points at y = 0 [-]

Q = ultimate uptake capacity of adsorbent [mol-C/kg]

Q_0 = parameter in Equation(3-12) [mol-C/kg]

q(x) = probability density of solid-phase TOC concentration [$(mol\text{-}C)^2/m^3kg$]

q_i' = solid-phase TOC concentration of i-component [mol-C/kg]

x = Langmuir coefficient in TOC concentration [m^3/mol-C]

y = accumulated amount of used adsorbent [kg/m^3]

<Greek letters>

α_n = parameter in Equation(3-15) [$(mol\text{-}C/m^3)^n$]

<Subscripts>

ad = adsorbable solute

calc = calculation

exp = experimental

unad = unadsorbable solute

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CHAPTER 4

APPROXIMATE DESCRIPTION OF MULTI-SOLUTE ADSORPTION RATE IN ORGANIC AQUEOUS SOLUTION

4-1 Introduction

The practical municipal or industrial wastewaters generally contain many kinds of pollutants, and in most cases their components and compositions are unknown. However most of studies for liquid phase adsorption, which have been proposed, deal with solutions whose solutes and compositions are known, so they can not be applied to wastewaters. An approximate description for adsorption equilibrium, which contains a new concept, "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration (C.D.C.)", has been proposed in the previous chapter. Using this description, it becomes possible to represent the adsorption equilibrium and

rate in terms of total concentration index of solutes in wastewater, for example TOC. In this chapter, an approximate description for adsorption rate of wastewater is proposed using the concept, C.D.C..

4-2 Identification of C.D.C.

In the previous chapter, it was assumed that the C.D.C. could be represented by Equation(3-9).

$$C(x,y) = C_T(0)G(x)\exp\{-f(y)xH(x)\} \qquad (3\text{-}9)$$

where

$$G(x) = a_1 x e^{b_1 x} \qquad (3\text{-}35)$$

Equation(3-35) is the form which is adopted only the second term (n = 1) of Equation(3-14), and it will be used in this chapter, because it was used at the calculation in the previous chapter. Equation(3-15) is also rewritten as Equation(3-36) because of the same reason, and it will be used here.

$$H(x) = 1 + \alpha_1 x + \alpha_2 x^2 \qquad (3\text{-}36)$$

The simulating formulas of C.D.C., Equations(3-9), (3-35) and (3-36), are those of Method I in the previous chapter, and they are also used in this

chapter, because Method I gave us the best results in the previous one. The differential adsorption equilibrium curve (D.A.E. curve) was used to identify the C.D.C., and the relationship between the D.A.E. curve and the C.D.C. was represented by Equations (3-10) and (3-13).

$$C_T(y) = C_T(0)\int_0^\infty G(x)\exp\{-f(y)xH(x)\}dx \qquad (3\text{-}10)$$

$$\frac{\partial f(y)}{\partial y} = \frac{Q_0}{1+C_T(0)\int_0^\infty G(x)\exp\{-f(y)xH(x)\}xdx} \qquad (3\text{-}13)$$

Because the function f(y) in Equation(3-9) is dependent on the D.A.E. curve through Equations(3-10) and (3-13), the parameters, Q_0, f(0), a_1, b_1, α_1 and α_2 must be determined from the D.A.E. curve to identify the C.D.C. as mentioned in Chapter 3.

The proposed description method (Method I) was compared with the lumped parameter method, Method III, in the previous chapter to verify its availability. In Method III, the solutes in wastewater were considered to consist of one unadsorbable solute and one adsorbable solute, which obeyed the Langmuir type adsorption. By Method III, the three parameters, K_{0c}, x_{ad} and Q_{ad}, in Equations(3-31), (3-32) and

(4-1) are determined from the D.A.E. curve.

$$C_T(y) = C'_{ad}(y) + C'_{unad}(0) \tag{3-31}$$

$$\frac{dC'_{ad}(y)}{dy} = - \frac{Q_{ad}x_{ad}C'_{ad}(y)}{1+C'_{ad}(y)x_{ad}} \tag{3-32}$$

$$K_{0c} = C'_{ad}(0)/C'_{unad}(0) \tag{4-1}$$

In this chapter, Method II in the previous chapter is not used, because Method I was more reliable than Method II in the previous chapter.

4-3 Theoretical Considerations

Here let us consider the rate of concentration change of the wastewater, whose C.D.C. is known, in a batch adsorption operation. The following assumptions are made.

1. Adsorbent particles are spherical.
2. Mass transfer resistance in liquid film is negligible.
3. Adsorption rate obeys the linear driving force approximation (L.D.F.A.) whose driving force is due to the gradient of solid-phase concentration.

For the single-solute adsorption rate, more exact

methods, in which the distribution of solid-phase concentration is considered, have been proposed[2,4]. In this chapter, however, the L.D.F.A., which has been proposed by Glueckauf[1] and used for the analysis of adsorption column[3] recently, is adopted in spite of its rough approximation, because the object of this chapter is to describe the rate of adsorption of unknown multi-components and so it is difficult to apply the more exact method for this case. Assumptions 1. and 2. agree with the experimental conditions as mentioned in 4-4.

In Chapter 3, the author proposed a concept of C.D.C. to describe the adsorption equilibrium of multi-solute system, and the purpose of this chapter is to extend the concept of C.D.C. to the adsorption rate of multi-solute system. When L.D.F.A. is adopted, the adsorption rate equation is represented by the product of $k_s a$ and the driving force. Since the driving force is represented by C.D.C. of the original solution, $k_s a$ can be assumed to be a function of x. This function, $k_s a(x)$, is dependent on adsorbates and adsorbent. This method is called Method I and this is consistent one to Method I in previous chapter as written in 4-2.

From the above descriptions, the following rate equation is obtained.

$$dq(x,t)/dt = k_s(x)a\{q^*(x,t)-q(x,t)\} \quad (4-2)$$

Equation(4-3) is derived from the material balance of batch adsorption process.

$$C(x,t) = C(x,0) - Aq(x,t) \quad (4-3)$$

Further the Markham-Benton equation, which is an extension of the Langmuir equation to multi-solute system, is represented by Equation(3-3).

$$q(x) = Q(x)C(x)x/\{1+\int_0^\infty C(x)xdx\} \quad (3-3)$$

Finally we can obtain the next equation from Equations (4-2), (4-3) and (3-3).

$$dq(x,t)/dt = k_s(x)a[Q(x)x\{C(x,0)-Aq(x,t)\}$$
$$/\{1+\int_0^\infty (C(x,0)-Aq(x,t))xdx\}-q(x,t)] \quad (4-4)$$

where Q(x) can be represented by Equation(4-5), using Equations(3-12) and (3-36).

$$Q(x) = Q_0H(x) = Q_0(1 + \alpha_1x + \alpha_2x^2) \quad (4-5)$$

Equation(4-6) is the initial condition of Equation(4-4).

$$q(x,0) = 0 \quad (4-6)$$

The initial C.D.C., C(x,0), and Q(x) can be obtained by Equations(3-9) and (4-5) using the parameters

which are determined from the observed D.A.E. curve as described in the previous chapter. Further the total concentration change is represented by Equation(4-7) from the integration of Equation(4-3).

$$C_T(t) = \int_0^\infty C(x,t)dx = C_T(0) - A\int_0^\infty q(x,t)dx \qquad (4\text{-}7)$$

In practical calculation for determination of $k_s(x)a$, in Equations(4-2) or (4-4), Equation(4-8) was adopted as a simulating formula, conveniently.

$$k_s(x)a = \beta_0 + \beta_1 x + \beta_2 x^2 \qquad (4\text{-}8)$$

In this case, the parameters to be searched are three, that is, β_0, β_1 and β_2. Giving the appropriate values for β_0, β_1 and β_2, we can numerically solve the differential equation, Equation(4-4), with C(x,0), Q(x) and Equation(4-6). By substitution of q(x,t) obtained here into Equation(4-7), $C_T(t)$ can be calculated. By searching optimal values of these parameters so as to fit $C_T(t)$ to the observed concentration change, we can identify $k_s(x)a$. The parameters were searched by SIMPLEX method using Equation(4-9) as the performance index.

$$F = -\sqrt{\sum_{i=1}^{N} [\{1-C_{Ti,calc}(t)/C_{Ti,exp}(t)\}^2 C_{Ti,exp}(t)]/N} \qquad (4\text{-}9)$$

On the other hand, Method III is considered in this chapter to compare with Method I. Method III is consistent to Method III described in the previous chapter as written in 4-2. Using Method III, the next equations describe the relationship between volumetric coefficient of intraparticle mass transfer of an adsorbable solute and the rate curve of concentration change.

$$dq'_{ad}(t)/dt = k_{s,ad}a[Q_{ad}x_{ad}\{C'_{ad}(0) - Aq'_{ad}(t)\} /\{1 + (C'_{ad}(0) - Aq'_{ad}(t))x_{ad}\} - q'_{ad}(t)] \quad (4\text{-}10)$$

$$q'_{ad}(0) = 0 \quad (4\text{-}11)$$

$$C_T(t) = C_T(0) - Aq'_{ad}(t) \quad (4\text{-}12)$$

As x_{ad}, Q_{ad} and K_{0c} can be determined from D.A.E. curves and $C_T(0)$ can be obtained by the rate experiment, another parameter $k_{s,ad}a$ can be determined from the rate curve of concentration change. The determination of the parameters was also performed by SIMPLEX method using Equation(4-9) as the performance index.

4-4 Experiments

The experiments were performed using two kinds of synthetic wastewaters. They were the aqueous solutions which respectively solved cyclohexanol, phenol, benzene, aniline, p-cresol and p-nitrophenol (0.167 : 0.167 : 0.166 : 0.167 : 0.166 : 0.167, mol fraction based on mol-C)(Wastewater I), and p-chlorophenol, p-cresol, nitrobenzene, m-nitrophenol and β-dinitrophenol (0.141 : 0.282 : 0.211 : 0.253 : 0.113, mol fraction based on mol-C)(Wastewater II). Activated carbon, X-7000, (10 ∿ 12 mesh, average diameter 1.54mm) from Takeda Chemical Industry Limited whose shape was spherical, was used as adsorbent. The procedure of the differential adsorption experiment for the determination of C.D.C. was completely the same as the previous chapter. The activated carbon particles were pulverized in ball mill, and the powdered carbon under 200 mesh was used. The experiment for adsorption rate was performed in the agitated tank made of glass as shown in Figure 4-1. The liquid volume was 1.3ℓ and the carbon particles (about 4g) were held in the basket made of stainless steel wire mesh. The solution was agitated by the impeller whose speed was more than 1100r.p.m. to make the condition of negligible mass

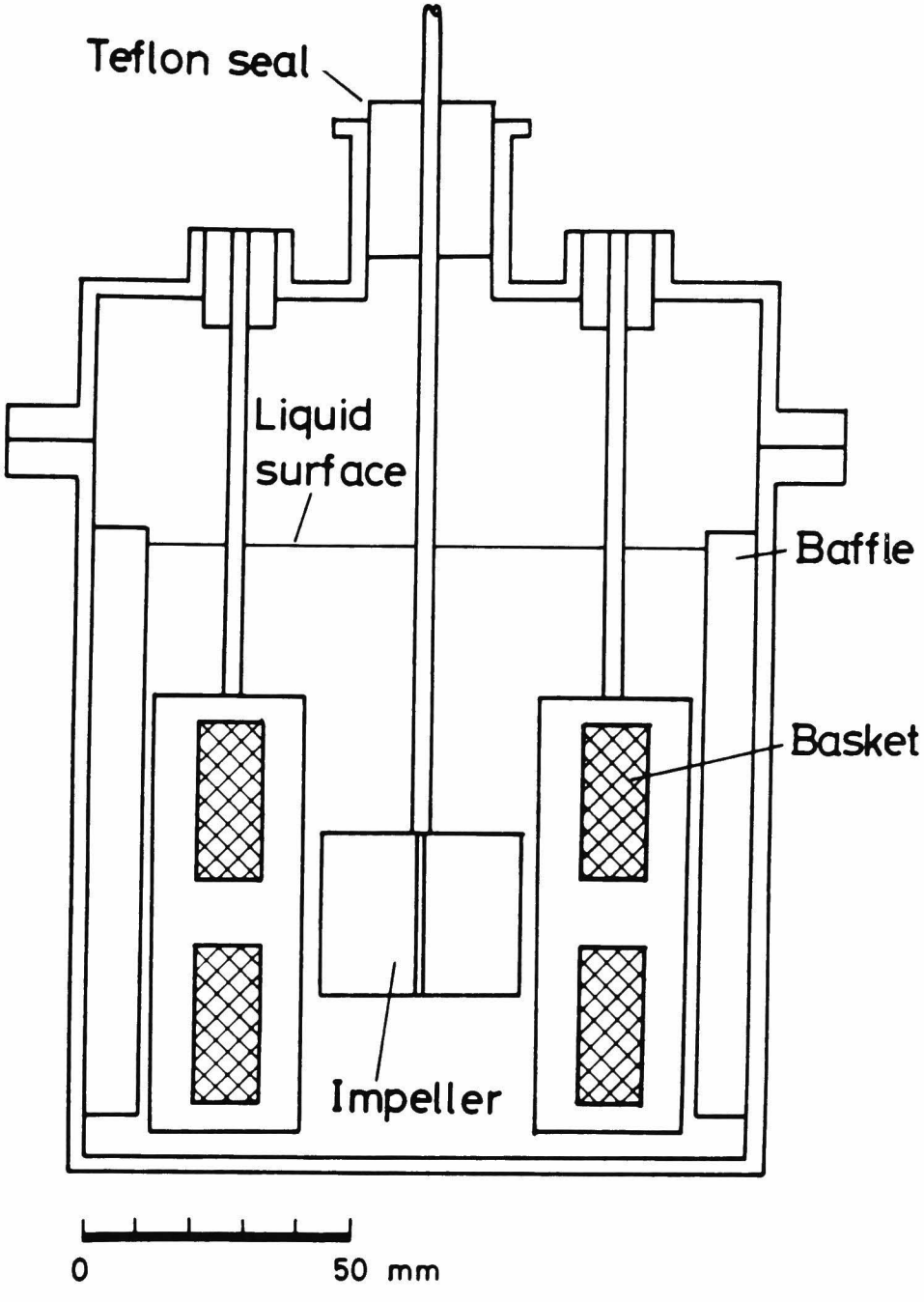

Fig.4-1 Shematic illustration of the reactor

transfer resistance between liquid and the surface of the particles. Sampling the solution from the tank periodically, the concentrations were measured by TOC analyzer. The temperature was 35°C for all experiments. Two rate curves of concentration changes, which had different initial concentrations, were measured for each wastewater, and the higher concentration curve was used for the identification of $k_s(x)a$ and $k_{s,ad}a$, and the lower one was used for the comparison with the prediction results.

4-5 Results and Calculation Procedures

The experiments were performed for Wastewater I and II, and the observed D.A.E. curves are shown in Figures 4-2 and 4-3. Two D.A.E. curves were also measured for each wastewater as done in Chapter 3. The parameters of Method I and III were determined from the two observed D.A.E. curves in the same way introduced in the previous chapter, and the values of the obtained parameters are represented in Table 4-1. The D.A.E. curves calculated by the uses of the parameters in Table 4-1, are shown in Figures 4-2

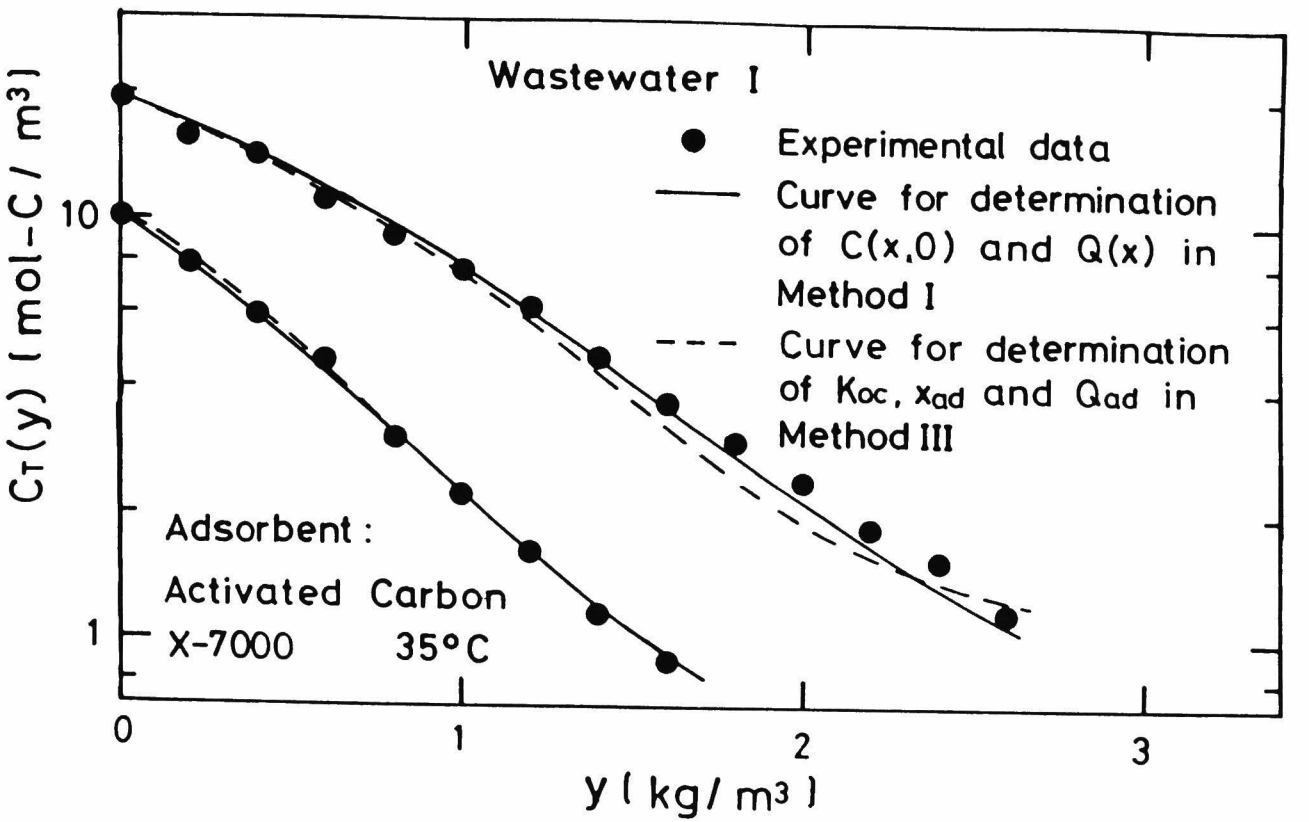

Fig.4-2 Differential adsorption equilibrium curves

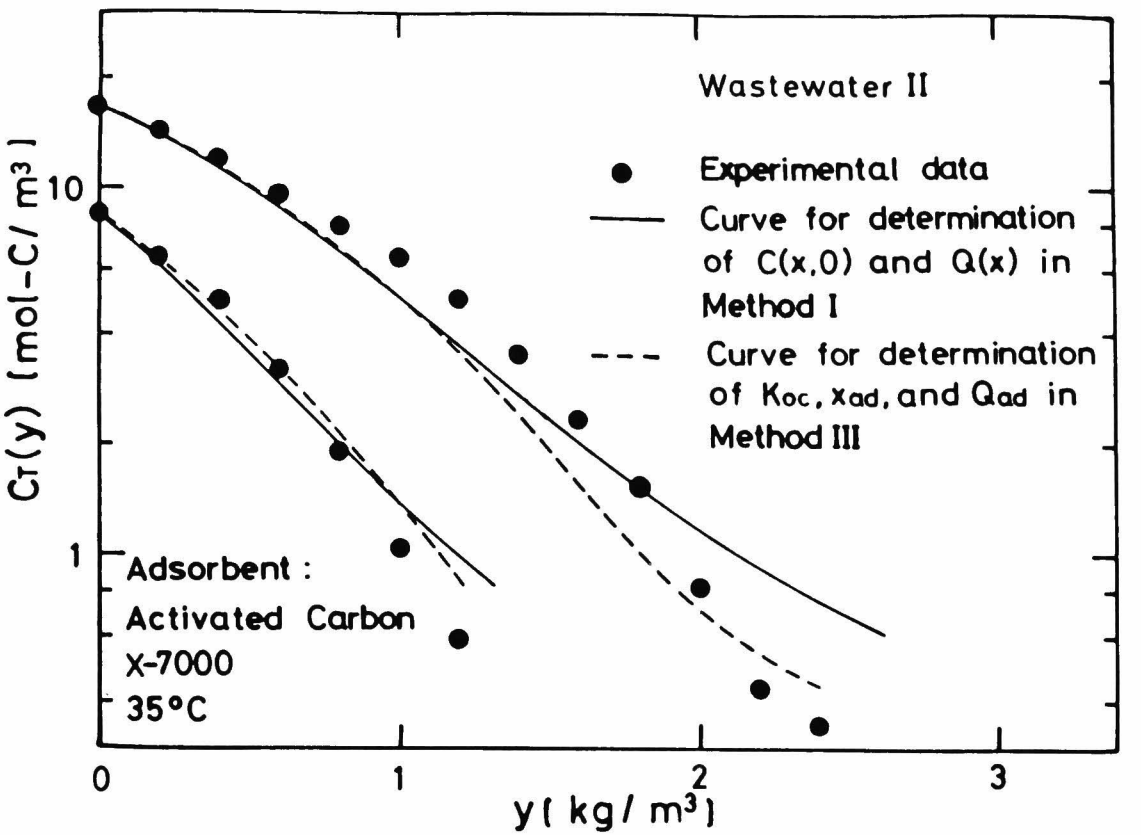

Fig.4-3 Differential adsorption equilibrium curves

Table 4-1 Parameters and Accuracies of Each Method

Wastewater	I	II
Method I		
a_1	46.46	51.52
b_1	0.1992	-0.3051
α_1	0.1035	-0.1176
α_2	0.01453	0.1192
Q_0	15.17	17.78
f(0)	6.695	7.015
Fitting accuracy* of D.A.E. curve	0.0300	0.2278
β_0	1.898×10^{-6}	6.342×10^{-5}
β_1	4.454×10^{-4}	1.424×10^{-4}
β_2	2.003×10^{-3}	1.815×10^{-3}
Fitting accuracy of curve* of concentration change	0.0273	0.0380
Prediction accuracy of curve* of concentration change	0.1023	0.0647
Method III		
K_{0c}	15.84	109.4
x_{ad}	0.1599	0.1447
Q_{ad}	18.63	19.93
Fitting accuracy* of D.A.E. curve	0.0553	0.1750
$k_{s,ad}{}^a$	2.041×10^{-4}	2.316×10^{-4}
Fitting accuracy of curve* of concentration change	0.1340	0.1508
Prediction accuracy of curve* of concentration change	0.2431	0.1714

* $F = (1/N) \sum_{i=1}^{N} (|C_{Ti,calc} - C_{Ti,exp}|/C_{Ti,exp})$

N : No. of experimental points

and 4-3. Further using the experimental D.A.E. curves and the fitting ones in Figures 4-2 and 4-3, the fitting accuracies for Method I and III were calculated by Equation(3-42).

$$F_a = (1/N) \sum_{i=1}^{N} (|C_{Ti,calc} - C_{Ti,exp}|/C_{Ti,exp}) \quad (3\text{-}42)$$

The results are shown in Table 4-1. The procedures of the above calculations have been explained minutely in 3-4.

The experimental results of adsorption rate for Wastewater I and II are shown in Figures 4-4 and 4-5. The experiments were performed using two systems which have different initial concentrations for each wastewater. The rate curve of concentration change, which had the higher initial concentration in the two curves, was used to determine $k_s(x)a$ of Method I and $k_{s,ad}a$ of Method III.

In this calculation, for Method I the following calculation was performed to obtain the parameters, β_0, β_1 and β_2. C(x,0) can be obtained by Equations (3-9), (3-35) and (3-36) using the parameters, a_1, b_1, α_1, α_2 and f(0) and the observed $C_T(0)$. On the other hand, Q(x) can be calculated by Equation(4-5)

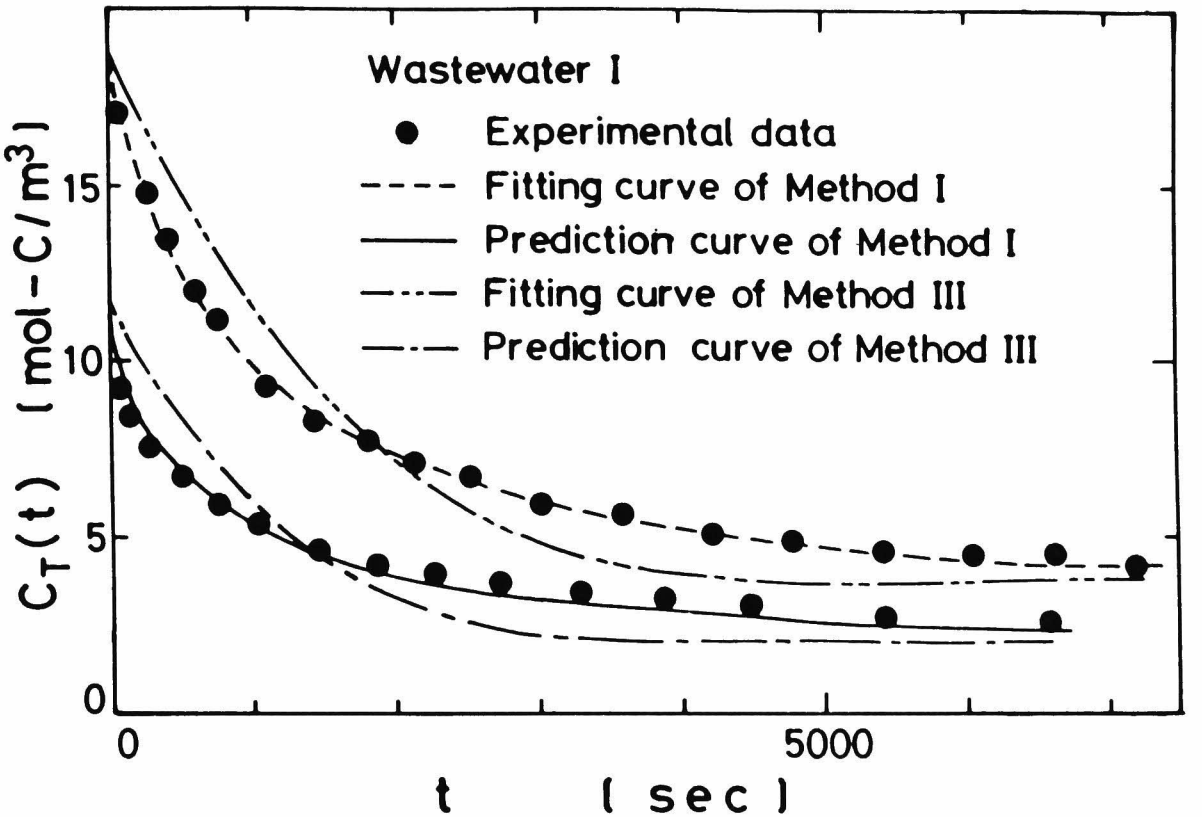

Fig.4-4 Rate curves of concentration change

(adsorbent : activated carbon X-7000, 35°C)

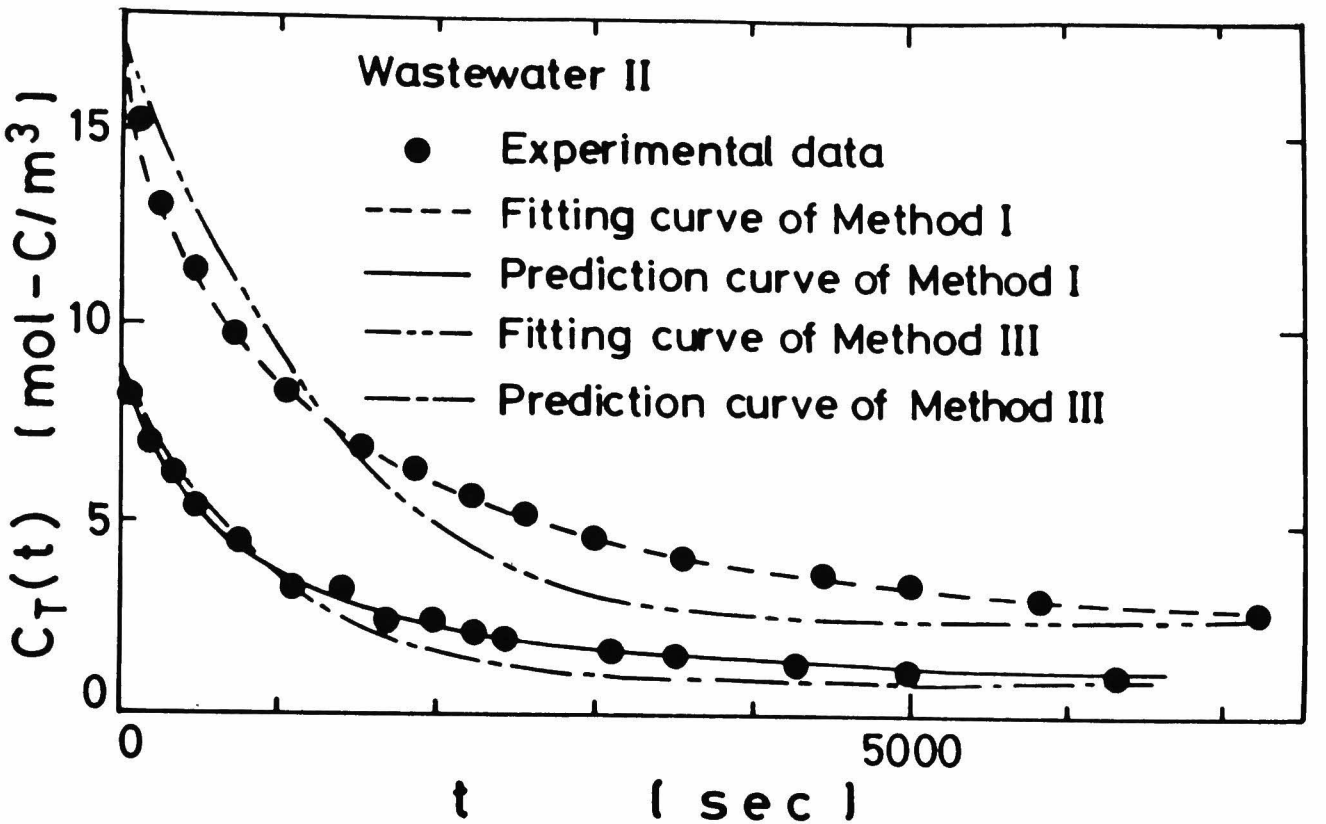

Fig.4-5 Rate curves of concentration change

(adsorbent : activated carbon X-7000, 35°C)

and the parameter, Q_0. Therefore giving the appropriate values of β_0, β_1 and β_2, $k_s(x)a$ can be obtained by Equation(4-8), and for a given amount of adsorbent, A, the differential equation, Equation (4-4), is solved by Runge-Kutta-Gill method with the initial condition, Equation(4-6). When the obtained $q(x,t)$ is substituted into Equation(4-7), we can get the curve of $C_T(t)$. Then we can finally identify $k_s(x)a$ by the searching of the optimal values of β_0, β_1 and β_2 so as to fit $C_T(t)$ to the observed $C_T(t)$ curve. The parameters were searched by SIMPLEX method using Equation(4-9) as the performance index.

The obtained optimal values of β_0, β_1 and β_2 are shown in Table 4-1 and the $C_T(t)$ curves calculated by the uses of the parameters in Table 4-1, are indicated in Figures 4-4 and 4-5. Further the fitting accuracies were calculated by Equation(3-42) and the results are also shown in Table 4-1.

In the case of Method III, when the appropriate value of $k_{s,ad}a$ is assumed for a given A, Equation(4-10) can be solved by Runge-Kutta-Gill method with the initial condition, Equation(4-11). Then $C_T(t)$ can be calculated with the substitution of the obtained $q'_{ad}(t)$ into Equation(4-12). The optimal value of

$k_{s,ad}a$ is searched by SIMPLEX method with the performance index, Equation(4-9), so as to fit $C_T(t)$ to the observed one.

The obtained optimal values of $k_{s,ad}a$, the $C_T(t)$ curves calculated by the uses of these values of $k_{s,ad}a$ and the fitting accuracies obtained by Equation(3-42) are respectively shown in Table 4-1 and Figures 4-4 and 4-5 similarly to Method I.

Next $C_T(t)$ curves of Wastewater I and II, which were corresponding to the experimental systems with the lower initial concentrations, were calculated by the uses of the obtained $k_s(x)a$ of Method I and $k_{s,ad}a$ of Method III.

For Method I, using Equations(3-9), (3-35), (3-36) and (4-4) to (4-8), the calculation for prediction was performed by Runge-Kutta-Gill method. For Method III, the prediction was performed using Equations(4-10) to (4-12) and Runge-Kutta-Gill method.

The prediction results for Method I and III are shown in Figures 4-4 and 4-5 by solid lines and chain lines with one dot, respectively.

4-6 Discussions

For the parameter fitting to the observed rate curve of concentration change, the fitting by Method I is performed with good accuracy as shown in Figures 4-4 and 4-5, so the simulating formula of $k_s(x)a$, Equation(4-8), is sufficient for the representation of $k_s(x)a$. In contrast to Method I, Method III does not give us good fitting accuracies.

Further we can find that the prediction result of Method I is much better than Method III for both wastewaters from Figures 4-4 and 4-5. The reason for the excellence of Method I can be thought that the distribution of k_sa, that is, $k_s(x)a$, is taken into consideration in Method I. The successful prediction of Method I shows us that the rough approximation, that is, the linear driving force approximation, is sufficiently usable in this description method.

Next let us compare the obtained values of $k_s(x)a$ with the proposed experimental data by Suzuki et al.[5], which were measured for various single organic solutes. The component corresponding to the value of x, which gives the maximum value of C of C.D.C.

for each wastewater, is regarded as the most influential solute in the adsorption system, and $k_s(x)a$ for this value of x is calculated. The value of $k_s(x)a$ is further converted into the effective surface diffusion coefficient, D_s, by the relationship, $k_s a \simeq 15 D_s / R^2$ [1], and we can get $D_s \simeq 4.51 \times 10^{-8}$ cm^2/s for Wastewater I and 4.70×10^{-8} for Wastewater II. On the other hand, Suzuki et al.[5] reported that the values of D_s for some of the organic solutes contained in these two wastewaters, were 2.9 - 16.× 10^{-8} cm^2/s. These values of D_s agree with ones obtained from $k_s(x)a$ in the same order, in spite of the difference of experimental conditions, so that the obtained $k_s(x)a$ is thought to be reliable.

The values of D_s obtained from $k_{s,ad}a$ of Method III are 8.07×10^{-8} cm^2/s for Wastewater I and 9.15×10^{-8} for Wastewater II, and they are a little greater than Method I.

As mentioned above, for the estimation of the adsorption rate of the aqueous solution which contains many unknown organic solutes, the proposed approximate description method (Method I) is useful. However it is desirable that the reliability of the description method will be further examined for many other adsorption systems.

4-7 Conclusions

1. The similar concept to the characteristic distribution of Langmuir coefficient for liquid concentration, which was proposed for the description of adsorption equilibrium characteristics of wastewater, was applied to the adsorption rate process, and a new approximate description of adsorption rate for wastewater was proposed with the linear driving force approximation.

2. By the approximate description, the rate curves of concentration change in a batch adsorption process were predicted exactly for the wastewaters whose characteristic distributions of Langmuir coefficient for liquid concentration were known.

3. Further, the values of volumetric coefficient of intraparticle mass transfer obtained by the approximate description, agreed with the experimental data of each solute in the same order.

4. As the accuracies of the fitting for the determination of parameters and the prediction of rate curve by Method III were much inferior to by Method I, it was found that we could not regard the solutes in wastewater as single solute to analyze the adsorption rate characteristic.

Nomenclature

A = amount of adsorbent used [kg/m^3]

a = specific surface area [m^2/kg]

a_1 = parameter in Equation(3-35) [$(mol\text{-}C)^2/m^6$]

b_1 = parameter in Equation(3-35) [$mol\text{-}C/m^3$]

C = probability density of liquid-phase TOC concentration [$(mol\text{-}C)^2/m^6$]

C' = liquid-phase TOC concentration [$mol\text{-}C/m^3$]

C_T = liquid-phase total TOC concentration [$mol\text{-}C/m^3$]

D_s = effective surface diffusion coefficient [cm^2/s]

F = performance index [$(mol\text{-}C/m^3)^{1/2}$]

F_a = fitting and prediction accuracy [-]

$f(y)$ = function of y in Equation(3-9) [$mol\text{-}C/m^3$]

$G(x)$ = function of x defined by Equation(3-35) [$mol\text{-}C/m^3$]

$H(x)$ = dimensionless function of x defined by Equation(3-36) [-]

K_{0c} = parameter in Equation(4-1) [-]

k_s = intraparticle mass transfer coefficient [$kg/m^2 \cdot s$]

$k_s a$ = volumetric coefficient of intraparticle mass transfer [1/s]

N = number of experimental points [-]

Q = ultimate uptake capacity of adsorbent [mol-C/kg]

Q_0 = parameter in Equation(3-13) [mol-C/kg]

q = probability density of solid-phase TOC concentration $[(\text{mol-C})^2/\text{m}^3\text{kg}]$

q' = solid-phase TOC concentration [mol-C/kg]

R = radius of adsorption particle [cm]

t = time [s]

x = Langmuir coefficient in TOC concentration $[\text{m}^3/\text{mol-C}]$

y = accumulated amount of used adsorbent $[\text{kg/m}^3]$

<Greek letters>

α_n = parameter in Equation(3-36) $[(\text{mol-C/m}^3)^n]$

β_n = parameter in Equation(4-8) $[(\text{mol-C})^n/\text{m}^{3n}\text{s}]$

<Superscript>

$*$ = at equilibrium

<Subscripts>

ad = adsorbable solute

calc = calculation

exp = experimental

unad = unadsorbable solute

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CHAPTER 5

CONCLUSIONS AND PROBLEMS IN FUTURE WORKS

CHAPTER 2

In Chapter 2, a Langmuir type single-solute adsorption equilibrium model for heterogeneous surface of adsorbent was proposed. The two parameters, which were involved in the model, were derived from the equilibrium data. Further the model was extended to multi-solute system, and two-solute adsorption equilibria were predicted by the use of parameters for single-solute system.

The prediction accuracy of proposed method for two-solute system was the same or a little better than two modified Radke's methods, which were proposed by Jossens et al. and derived by the application of the thermodynamics of ideal dilute solution to the adsorbed phase.

CHAPTER 3

In this chapter, an approximate description, which was based on the new concept, "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration", was developed to describe the adsorption equilibrium of wastewater whose components were numerous and unknown in terms of such a comprehensive index of concentration as TOC, BOD or COD.

The prediction accuracy was demonstrated through the adsorption experiments of five kinds of synthetic and industrial wastewaters. The prediction results agreed well with the experimental data and the propriety of the proposed description was confirmed.

The concept, "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration", which was proposed in the derivation of the approximate description, may also be thought to be useful for analysis or design of separation or reaction processes which are concerned with unknown multi-component systems. Further using the characteristic distribution of Langmuir coefficient, it is possible not only to predict the adsorption equilibrium but also to evaluate the adsorption characteristic of adsorbent such as activated carbon.

CHAPTER 4

In Chapter 4, the same concept to the characteristic distribution of Langmuir coefficient for liquid concentration which was proposed for the description of adsorption equilibrium of wastewater, was applied to the adsorption rate process, and a new approximate description of adsorption rate for wastewater was proposed with the linear driving force approximation. The rate curves of concentration change of wastewaters for batch adsorption process were predicted exactly by the approximate description, and the obtained volumetric coefficients of intraparticle mass transfer agreed with the experimental data in the same order.

Problems in Future Works

For the theme of Chapter 2, the deviation of prediction values might be owing to the affinity among adsorbate molecules, as mentioned in 2-5-2, so the study for this problem is very interesting and it might give us many useful informations for the modification of prediction method.

As Chapter 3 and 4 are the fundamental steps to the establishment of the procedure of the design of

adsorption equipments for wastewater, the results obtained in Chapter 3 and 4 are very useful to accomplish the purpose. However, we will encounter some following problems on the way to the goal. Because the information obtained by adsorption equilibrium, is affected remarkably by the behavior of the more adsorbable solutes, the characteristic distribution of Langmuir coefficient for liquid concentration identified by the differential adsorption equilibrium curve, might be exact in the higher range of the Langmuir coefficient, but in the lower range it might be in some measure inexact. On the other hand, the prediction of the breakthrough curve requires the accuracy of the characteristic distribution of Langmuir coefficient for liquid concentration in the lower range of the Langmuir coefficient, because the less adsorbable the component is, the earlier it arrives at the breakthrough point of the fixed adsorption column. So the accurate characteristic distribution of Langmuir coefficient especially in the lower range of the Langmuir coefficient, is necessary to predict the breakthrough curve more exactly.

It is also necessary for the characteristic

distribution of Langmuir coefficient for liquid concentration approximated by the following equation to be modified by development of mathematical procedure.

$$C(x,y) = C_T(0)G(x)\exp\{-f(y)xH(x)\} \qquad (3\text{-}9)$$

When we can get the accurate characteristic distribution of Langmuir coefficient for liquid concentration, it becomes possible to be used more extensively as one of the important indexes which describe the adsorption characteristics of adsorbent.

Further, as the concept of "Characteristic Distribution of Langmuir Coefficient for Liquid Concentration", can serve to the analysis or design of separation or reaction processes which are concerned with unknown multi-component systems, the application of this concept to many other fields can be expected in the future.

POSTSCRIPT

This thesis is a collection of some works for adsorption in liquid phase which were performed by author in 1975 to 1979 at the laboratory of Professor R. Toei of Kyoto University.

These works mainly deal with the adsorption from relatively dilute solution which involves many components. The aim of this field may be to establish the procedure of the design of adsorption equipments for wastewater, and this thesis exists at the entrance of the way to the aim.

Author hopes that the further study will be performed and that the purpose will be accomplished.

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Kyoto, September 1980